

CHEMICAL ABSTRACTS

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1—APPARATUS

C. G. DERICK

Tools of the chemical engineers. I. Agitators. D. H. KILLEFFER. *Ind. Eng. Chem.* 15, 144-8(1923).—Agitators are classified as (1) paddles, (2) turbines, (3) propellers, (4) moving vessels, (5) combinations of the above, (6) miscellaneous. The article is descriptive only.

W. L. BADGER

Report of committee D-10 on shipping containers. J. A. NEWLIN, et al. *Proc. Am. Soc. Testing Materials* 22, I, 483-5(1922).—Report of progress in standardizing various containers.

C. C. DAVIS

The problem of carboy closure. ANON. *Chem. Met. Eng.* 27, 1267-8(1922).—Carboys with chipped or cracked necks may be reclaimed by grinding the necks sufficiently to make the surface smooth. The app. is illus. and its operation explained. The smooth surface means a saving of plaster of Paris; it is cleaner; better closure is obtained; and disputes between buyer and seller are eliminated. The cost of reclamation is 10 c. per carboy.

W. H. BOYNTON

Roth's rotary cock. ANON. *Chem.-Ztg.* 46, 1037(1922).—The cock is turned by a wheel below which is a small lock wheel. The hole through the plug is very wide, to avoid blocking, and may be cleaned out by removing a cover at the bottom of the body.

J. H. MOORE

A torsion viscosimeter for the study of lyophilic sols. I. N. KUGELMASS. *Compt. rend. soc. biol.* 87, 885-8(1922).—The app. consists of 3 parts: an oscillatory system, a rotating system, and an observation system. The first is made from a Ni-plated brass sphere 2 cm. in diam. attached to a brass rod (also Ni-plated) 18 cm. long to which is attached a small mirror. The rod is fastened to a phosphorbronze wire 18 cm. long and 1 mm. in diam. The 2nd system is made from a silvered Dewar tube set into a stand of an elec. driven kymograph. The position of the mirror is detd. by means of a telescope arrangement provided with a scale. The lyophilic sol under examn. is placed in the Dewar tube and the ball of the oscillatory system is submerged in the material. The Dewar tube is now rotated at a rate of about 1 revolution per 10-15 sec. and the deviation of the mirror measured with the telescope. The viscosity is calcd. from these data, viz., that it is directly proportional to the product of the time required for 1 revolution by the max. mean deviation of the sphere ($t \times d$). The following sources of error must be taken into consideration. The angular velocity: this factor is eliminated by not making the 'rate' of rotation too rapid. Deviation of the sphere: after each detn. the mirror should return to the zero point. Temperature: all the readings must be made at the same temp. Rigidity of surface of the sol: the surface should be carefully broken up before each new detn.

S. MORGULIS

The Michell viscosimeter. J. L. *Technique moderne* 14, 360-1(1922).—The viscosimeter consists essentially of a metal cup and a metal ball fitting very accurately in the cup. The cup is provided with 3 small projections, so that the distance between the ball and cup is accurately known (of the order of 0.01 mm.). The cup is provided with a hollow handle for the insertion of a thermometer. To carry out a detn., pour a few drops of oil in the cup, place the ball and press it firmly into the cup, reverse the

position of the instrument, and note the time required for the sphere to fall. The time multiplied by the const. of the instrument gives directly the viscosity in dynes per cm.² Detns. with this app. agree closely with those obtained with the Redwood viscosimeter. The Michell detns. required two hours and the Redwood nearly two days. The theory of the instrument is briefly explained. A. P.-C.

The "Davon" micro-telescope and supermicroscope. F. DAVIDSON. *Chem. News* 125, 353-5(1922).—This instrument can be utilized as a telescope or microscope. When used as the latter its working distance is greater than that with an ordinary microscope. D. E. SHARP

A new crucible for the rapid determination of sulfur. HEINRICH HILLER. *Z. angew. Chem.* 36, 25-6(1922); 3 cuts.—A modification of Parr's crucible and method (C. A. 13, 782) to make them applicable to the detn. of S in oil products of widely varying sp. gr. About 1 g. of powd. KClO₃ is put in the Fe crucible, 0.3 g. of the substance weighed in and mixed well with the KClO₃, about 10 g. of Na₂O₂ added, and the whole mixed, the lid clamped on, the charge ignited by heating the bottom of the crucible for 1 min. with the tip of a blast, the crucible cooled in H₂O at once, the contents are dissolved and S is pptd. as BaSO₄. J. H. MOORE

Filter employed in working with membrane filters. GERHART JANDER. *Z. angew. Chem.* 35, 721-2(1922).—A description, with 1 cut, of a new ring-clamp for holding membranes on Zsigmondy's filter, by the use of which breakage of the filter is practically eliminated. J. H. MOORE

The wear of alcoholometers. R. MARCILLÉ. *Ann. fals.* 15, 462-3(1922).—Alcoholometers (weighing about 75 g.) which had been used constantly for a long time lost 38 mg. and 58 mg., owing to wearing of the weighted tip; this caused an error of +0.2-0.3% alc. by vol. The loss can be corrected by adding a drop of easily fused glass at the top of the stem and grinding off the excess. A. P.-C.

Determinations of water content by a new rapid water-determination apparatus of S. H. Meihuizen. K. MOUS. *Chem.-Ztg.* 46, 649-51(1922).—An app. for the rapid detn. of H₂O in finely divided substances is described. It is particularly recommended for grain and malt products. The method consists essentially in drying at a const. temp. by means of a boiling liquid. A vertical tube, approx. 420 mm. high and 53 mm. diam., open at the top, contains a frame for several weighing cups to hold the substance. A larger tube 25 mm. deeper surrounding the inner one contains approx. 75 cc. of the liquid of desired b. p. The upper part of the space between the 2 tubes is filled with broken glass or stone serving as an air-cooled condenser for the vapor. Through the bottom of both tubes passes a bent tube approx. 18 mm. diam., through which passes into the inner tube a current of air previously dried with H₂SO₄. The outer vertical tube is air insulated by a surrounding jacket. Heat is furnished at the bottom. Drying may be effected by H₂O at 99°, by xylene at 139°, etc. Approx. 3 g. of substance are placed in each weighing cup, which can be covered after drying. Molasses, sugar, cocoa, starch, dextrin, cheese, bread, dried milk, glue, clay, etc., can be dried in 50 min. at 139°. Substances not decompd. at 139° can be dried in 15 min. by xylene in place of H₂O. In this case the air need not be dried, for the error is only a few 100ths %. (Cf. German patent 309,982). C. C. DAVIS

A double hook support for watch glasses. G. F. SMITH. *Ind. Eng. Chem.* 15, 248(1923); illus. E. J. C.

Standard Specifications for Laboratory Apparatus Adopted by the Manufacturing Chemists' Association of the United States., Part I. Graduates and Thermometers. Washington, D. C.: Mfg. Chemists' Assoc. of the U. S. 49 pp. \$1.50. Reviewed in *Ind. Eng. Chem.* 15, 214(1923).

Condenser. S. GURSKI. U. S. 1,440,917, Jan. 2. A condensing coil is placed within a casing contg. air which may be renewed or exhausted by a bellows. The casing is surrounded by a jacket for H_2O or other cooling medium. The air chamber around the condensing coil serves to regulate the cooling of the coil.

Apparatus for conducting gas reactions at controlled temperatures. C. CONOVER. U. S. reissue 15,520. Jan. 9. (Original pat. 1,324,443; C. A. '14, 369). Reaction chambers of relatively shallow construction superposed one above another are each provided with cooling compartments above and below, contg. cooling mediums of different b. ps.

Apparatus for absorbing and recovering gases. FARBWERKE VORM. MEISTER, LUCIUS, & BRUNING. Brit. 187,223, Oct. 10, 1922. App. in which gases are absorbed by means of charcoal and recovered therefrom, and in which the charcoal is prepd. for re-use, is so constructed that these steps are performed in one continuous operation.

Perforated filler plates for gas reaction towers. W. H. ROSE. U. S. 1,412,414, Jan. 16. Superposed nested shallow dish-like sections are formed with concentric grooves in their bottoms from which inclined passages extend through the bottom. These baffle or reaction plates may be formed of stoneware, earthenware or other acid-resisting material.

Apparatus for separating gas from oil. H. WIRSHING. U. S. 1,440,197, Dec. 26.

Apparatus for sterilizing by impact. V. L. EMERSON. U. S. 1,440,868, Jan. 2. *Serums, exts., foods* or other liquids to be sterilized are confined within a chamber adapted to withstand considerable pressure and subjected to concussive impact by the action of a plunger.

Gas-sampling device. E. A. CLARK. U. S. 1,441,066, Jan. 2. Two pairs of receptacles are connected so that suction may be created in 2 of the receptacles by permitting liquid to flow into the other two.

Pulp filter for filtering gas-charged beverages. E. ZAHM. U. S. 1,439,721, Dec. 26.

Apparatus for drying fruits, vegetables, drugs or other materials. J. SCHNEIBLE. U. S. 1,442,179, Jan. 16. The material undergoing drying is supported on superimposed trays within an annular drying chamber in which a circulation of air is maintained.

Reinforced receptacles for packaging formaldehyde or other solutions. L. M. WHITE and J. A. FISH. U. S. 1,440,571, Jan. 2.

Ball testing apparatus for estimation of resiliency of metals, rubber or other materials. R. M. GASTON. U. S. 1,441,626, Jan. 9. A steel ball is held by a magnet and released from a definite height and allowed to fall upon the material under test and the rebound of the ball is noted.

Pyrometer of the potentiometer type. H. J. BLAKESLEE. U. S. 1,441,207, Jan. 9.

Thermionic valves; producing electric oscillations. GENERAL ELECTRIC CO. Brit. 184,903, May 25, 1921. A discharge device having as electrodes only an anode and an electron-emitting cathode contains a vapor or an inert gas such as He at a pressure below 1 mm. of Hg and such that the device exhibits a negative amp. v. char. ω characteristic over a part of its operating range. A suitable pressure is 5-75 microns ω Hg.

Electric discharge devices; producing high vacua. GENERAL ELECTRIC CO., LTD. AND N. R. CAMPBELL. Brit. 187,055, July 28, 1921. A high vacuum in a vessel, e. g., a thermionic rectifier or Röntgen-ray tube, is maintained by "gettering" action produced in an auxiliary vessel in gaseous connection with the main vessel. The "getter" consists of a substance contg. P, S, I or As, and is deposited on the walls of the auxiliary vessel when, or before, an elec. discharge is started in that vessel, and the "gettering" action is the process of causing a discharge to pass through the auxiliary vessel after the "getter" is deposited, the gas removed by the action being deposited on the walls.

The discharge may be produced by electrodes, or preferably, by means of an incandescent filament coated with the "getter," the leading-in wires and the ends of the filament forming the electrodes. More than one auxiliary vessel may be used. Cf. 11,539, 1909 and 1218, 1913.

2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

This year's Nobel prize winners. O. KLEIN. *Teknisk Tids.* 52, Uppl. A, 827-32 (1923).—About the work of Einstein, Bohr, Soddy, and Aston. The efforts of each are taken up separately and the relations between the ideas of the 4 men are excellently brought out. Portraits. A. R. ROSE

Chemistry as an aid in the detection of crime. HENRY LEFFMANN. *Am. J. Pharm.* 94, 691-9(1922).—A lecture. W. G. GARSSLER

Ancient history of the metals. E. O. VON LIPPMANN. *Swensk. Kem. Tids.* 34, 197-213(1923). A. R. ROSE

Models to illustrate a few principles of symmetry in teaching stereochemistry. ERNST MOHR. *J. prakt. Chem.* 105, 93-101(1922).—Several models are illustrated and described for demonstrating spatially (1) mols. which have, except for a four-fold combined rotation and reflection axis, and the resulting two-fold axis of simple symmetry, no elements of symmetry and (2) mols. having as the sole element of symmetry a center of symmetry. These models, unlike crystallographic or polyhedral ones, are easily and quickly made with simple lab. accessories, and emphasize the fact that not only are crystals, polyhedrons and point lattices subject to the laws of symmetry, but space diagrams of all kinds. C. C. DAVIS

The present significance of the atomic weights. T. W. RICHARDS. *Bull. soc. chim.* 31, 929-43(1922).—A lecture. J. A. ALMQUIST

Missing elements in the periodic table. II. F. H. LORING. *Chem. News* 125, 386-8(1922); cf. *C. A.* 17, 655.—The calcns. of Clarke and Washington on the relative distribution of elements in the earth's crust show that Sc exists in relatively small quantities compared with Ca and Ti, on each side of it. It is held that there is an at. no. series giving the periodic places where no elements can fall, or if they do fall, the quantities will be minute. The wedge type of periodic table involving at. levels as well as at. nos. is illustrated by a perspective drawing. III. *Ibid* 126, 1-4(1923).—The existence of Sc in the sun does not necessarily invalidate any relative quant. deduction as to the proportionate amts. of the element relative to those on each side of it in the at.-no. series, for the sun may be forming or degrading practically all the existing elements, and any excess of one in particular may not appear in large relative quantities in the final state when the process of formation and degradation is finished. JAMES M. BELL

The structure of crystalline mercury. N. ALSEN AND G. AMINOFF. *Geol. Förf. Förh.* 44, 124-8(1922).—Powder photographic data are recorded for cryst. Hg at the temp. of CO₂ snow. It is concluded that 4 atoms are contained within a hexagonal unit cell for which $a = 3.84 \text{ \AA. U.}$ and $c = 7.24 \text{ \AA. U.}$ The arrangement of these atoms is given by the coordinate positions: 000; 0, 0, $p \frac{1}{2}$; $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$; $\frac{2}{3}, \frac{1}{3}, p$, where the value of p is indeterminate. RALPH W. G. WYCKOFF

The crystal structure of hexamethylenetetramine. R. G. DICKINSON AND A. L. RAYMOND. *J. Am. Chem. Soc.* 45, 22-9(1923).—Laue photographic and spectrum photographic data from crystals of hexamethylenetetramine have been accounted for by a

structure composed of like molecules of $C_6H_{12}N_4$ in parallel orientation on a body-centered cubic lattice. The length of the edge of the unit cube is 7.02 Å. U.

RALPH W. G. WYCKOFF

The boiling points of ammonia, sulfur dioxide and nitrous oxide. F. W. BERGSTROM. *J. Phys. Chem.* **26**, 876-94(1922).—The b. ps. were measured in a vacuum-jacketed vessel, and in part of the work a modified Cottrell tube was employed. The b. p. of NH_3 detd. in a single-walled vessel is about 0.2° high. The following results for b. p. were obtained: NH_3 $-33.41^\circ \pm 0.1^\circ$; SO_2 $-10.02^\circ \pm 0.1^\circ$; N_2O $-89.5^\circ \pm 0.2^\circ$.

J. A. ALMQUIST

Passage of hydrogen through quartz glass. J. B. JOHNSON AND R. C. BURT. *J. Optical Soc. Am.* **6**, 734-8(1922).—The rate of flow of H_2 through quartz glass has been measured over the range from 300° to 900° . Some measurements were also made with N_2 and A. A perceptible diffusion starts with H_2 at about 300° and with the N_2 at 600° and then in each case increases rapidly with the temp. A well evacuated bulb of 1 l. capacity can be kept in air at 400° for 100 hrs. before the pressure, caused mostly by N_2 , reaches 10^{-4} mm. The transusion begins at a temp. at which structural changes are known to occur in cryst. silica; this suggests the possibility that passage of the gas may accompany a modification in the structure of the non-cryst. material. E. F. P.

A revised equation of state. A. W. PORTER. *Phil. Mag.* **44**, 1020-4(1922).—Dieterici's and Berthelot's equations of state are critically discussed and a modified equation is developed and applied to isopentane. At low pressures the new equation approximates closely to Berthelot's. At a pressure one half of the crit. P.'s equation fits exptl. results better than either van der Waals' or Dieterici's equations.

S. C. L.

The kinetic theory of an isolated saturated vapor phase. E. WERTHEIMER. *Z. Physik* **10**, 252-5(1922).—The relations between supersatd. vapor (a), satd. vapor (b), unsatd. vapor (c), and liquid (d), all at const. temp., are considered. The three vapor states are stable when no change in vol. occurs and no heat is exchanged with the surroundings. Then (1) $dS = 0$, where S is entropy, and a , b , and c differ only in their sp. vol., v . For b , (2) $v = f(T)$ only, but for a and c , v is a function of other variables besides T . In order to define kinetically the condition for satn. of a phase, equation (2) must be considered from the kinetic standpoint. Since the kinetic energy per mol., $L = \frac{3}{2} RT$, equation (2) can become (3) $L = f(v)$. From (3) the properties of a satd. vapor should be deducible. This would be possible if the law followed by the mols. due to their mutual fields of force and collisions were known, a law which it no longer appears to be impossible to det.

E. N. BUNTING

Vapor pressure of some copper-zinc alloys in the solid state. LEON CUILLEY AND MARCEL BALLÁY. *Compt. rend.* **175**, 1057-8(1922).—The velocity with which Zn volatilizes from Cu-Zn alloys varies with the nature of the surrounding atm. It is slower in air and O_2 than in N_2 , CO_2 and H_2 because of the formation of a coating of the oxide. The vapor pressures of an alloy contg. 55.2% Cu were detd. in H_2 atm. at 700-800°. Raoult's Law is not obeyed.

J. A. ALMQUIST

The form of the vapor-pressure curve at high temperature. I. The curve for lead. C. K. INGOLD. *J. Chem. Soc.* **121**, 2419-32(1922).—Since none of the formulas connecting vapor pressure and temp. developed so far has an entirely satisfactory theoretical basis it is important for the general theory of the fluid state of matter to exam. their applicability under more extreme conditions of temp. than the comparatively limited ranges to which they have been applied. The vapor pressure of Pb was measured by the dynamic method over the range 920° to 1340° . The Pb, purified by distn. under reduced pressure of N_2 , was boiled under varying pressures of N_2 in a porcelain or carbon tube heated in a special gas furnace, the upper part being cooled to act

as a reflux condenser. The temp. was measured by means of a Pt-Rh thermocouple placed in the vapor, which had previously been calibrated against a Pt resistance thermometer. Pressure was measured by a manometer attached to the cooler parts of the app. Measurements were made on both ascending and descending scales of pressure. The results are compared with the Kirchhoff-Hertz-Nernst formula, the formula of Henglein (*C. A.* 15, 198) and the empirical formula of Ramsay and Young, with Hg as the comparison liquid in the latter case and the data of Smith and Menzies (*C. A.* 5, 232) for the vapor pressure of Hg. Both the Nernst and the Henglein formulas differ from the exptl. values by an amt. considerably greater than the exptl. errors, while the empirical formula of Ramsay and Young is found to coincide with the observed results.

F. L. BROWNE

The application of Rast's camphor method to the micro-determination of the molecular weight of liquids. J. HOUBEN. *J. prakt. Chem.* 105, 27-30(1922).—The dissoln. of 1 mole of a substance in 1 kg. camphor depresses the f. p. of the latter 40°. By measuring, in capillary m-p. tubes, the f.-p. depression of camphor Rast was able to det. the mol. wt. of small samples of solids (*C. A.* 16, 2060). In using this method for detg. the mol. wt. of liquids a mixt. should be chosen of medium or small f.-p. depression. Thus, a mixt. of camphor and *n*-heptyl alc. having a f.-p. depression of 31° gave a mol. wt. 10 units high, whereas one of 14° depression gave the exact mol. wt. It was attempted to apply the method to liquids of low b. p. and low mol. wt. by dissolving a large amt. of the liquid in the camphor in order to depress the f. p. of the soln. as far as possible below the b. p. of the liquid, and thereby lessen the volatilizing of the liquid. This, however, was unsuccessful. The liquid of lowest b. p. (147°) for which data are given is acetylene tetrachloride. 0.0307 g. of this dissolved in 0.5375 g. camphor gave a f.-p. depression of 13°, and a mol. wt. of 176. The calcd. values are, resp., 13.6° and 168. Detus. on 11 other liquids having b. ps. between 175° and 345° gave mol. wts. differing from the calcd. values by 0-8 units.

R. H. LOMBARD

Molecular weight of the sodium-tellurium complex in liquid ammonia as derived from vapor-pressure measurements. C. A. KRAUS AND E. H. ZEITFUCHS. *J. Am. Chem. Soc.* 44, 2714-28(1922).—Results of measurements of the vapor-pressure lowering due to the complex Na-Te compd. in liquid NH₃ show that apparently Raoult's law is very nearly obeyed by solns. of the complex in this solvent, and that 2 atoms of Na are present per mol. of the complex. The complex telluride ion carries 2 charges. The formation of the complex telluride consists in the addition of Te atoms to the normal telluride ion, the valence of the latter remaining unchanged.

H. J. C.

Simple presentation of the general properties of colloids. W. M. BAYLISS. *Lancet* 1922, I, 38-40.—A brief review.

E. B. FINK

The dielectric constant of colloidal solutions. J. ÉRREIRA. *J. phys. radium* 3, 401-10(1922).—See *C. A.* 16, 4123.

HENRY C. PARKER

The preparation of the colloidal gold solution. ERNST-FRIEDLÄNDER. *Wiener klin. Wochschr.* 35, 975(1922).—F. warns against the use of K₂CO₃ contaminated with traces of the bicarbonate in the prepn. of the Au sol, which results in the production of CO₂ during the heating and consequent incomplete reduction of the Au. Pure samples of K₂CO₃ can be freed of traces of bicarbonate by gentle heating.

W. A. PERLZWEIG

Black colloidal suspensions in phosphorus. C. H. HALL, JR. *J. Am. Chem. Soc.* 45, 67-9(1923).—A bibliography of the literature relating to black phosphorus is given. By the Svedberg method of high-tension arcing under a liquid, colloidal solns. of Cu₃P₂ and of Hg in molten yellow P have been obtained. On cooling these give homogeneous black solids of sp. gr. about 1.9, which on extn. with CS₂ leave crystals of Cu₃P₂ or droplets of Hg. It is concluded that Thénard's "black phosphorus" is a colloidal soln. of Hg in P while Bridgman's material is a true allotropic modification.

F. L. BROWNE

Colloidal chemistry and meteorology. A. SCHMAUSS. *Kolloid Z.* 31, 266-9 (1922).—An address. A review of many of the properties of the atmosphere considered as an aerosol. The colloidal factors of stability of clouds, the causes of pptn. or rain are considered with small drops of water or ice as a sol in air. Thunder storms are traced to effects of dust which when electrically discharged produce lightning. The importance of colloid chemistry in weather forecasting and its bearings on meteorology in general are discussed.

A. MUTSCHELLER

The scattering of light by organosols and gels of cellulose acetate. F. W. J. MARDLES. *Trans. Faraday Soc.*, preprint 1922.—When a cone of light from an elec. lamp is passed horizontally just below the surface of a sol or gel in a nephelometer tube, scattered light passes up the tube. A quantitative measurement of this scattered light measures the *Tyndall number*. The amt. of light scattered by a chosen sample of castor oil at 20° was taken as unity. When a sol is cooled, the Tyndall number increases with increasing acceleration until a point of inflection is reached. This point of inflection occurs when the system has set to a firm jelly. When the gel is warmed the same sort of curve is formed but there is a shift due to hysteresis. This acceleration of the increase in Tyndall number, viscosity measurement, and the abnormal path of a sphere falling through such a system show that there is a gradual change from sol to gel. During this transition the gel structure is either fragile, or exists only in fragments. Slow cooling produces a smaller number of larger droplets of the internal phase. These gels may become opaque. Rapid cooling produces numerous very small droplets of the internal phase. These gels may be transparent. Stirring, together with rapid cooling, increases the Tyndall number. In an unstirred system, the Tyndall number increases rapidly with the concn. up to a max. of 0.06 for cellulose acetate in benzyl alc. Further increase in concn. causes a decrease in the Tyndall number. *Gelation* consists of 3 sep. processes: condensation, aggregation, and linkage. *Condensation* consists of the union of particles in a common film. *Aggregation* is the grouping of these larger particles close together but in sep. films.

F. E. BROWN

Viscosity changes associated with the gel-to-sol transition. F. W. J. MARDLES. *Trans. Faraday Soc.*, preprint 1922.—When a gel is warmed, at first there is a rapid decrease in viscosity which continues at a diminishing rate until a fairly const. viscosity is attained. In some particulars solution resembles the melting of a solid. However, the "melting point" of a gel is indefinite when detd. by the rate of fall of a steel ball, a stream line plunger, or a globule of Hg. The expts. were carried out with gels of cellulose acetate in benzyl alc. The relations between solution, temp., concn., previous history, and mechanical treatment are shown in 36 tables of data. The gels of higher concn. have higher "melting points." Gels which were permitted to stand overnight required more than twice the time needed for the same gels freshly prepd. Agitation hastens solution.

F. E. BROWN

The adsorption of toluene vapor on plane glass surfaces. F. K. CARVER. *J. Am. Chem. Soc.* 45, 63-7 (1923).—The adsorption of toluene vapor on plain surfaces of Pyrex glass at 0° and at pressures from 0.0006 to 0.2629 mm. of Hg has been studied with a view to throwing light on the question of the thickness of the adsorbed layer. The results agree with Langmuir's adsorption formula and indicate that the adsorbed layer is not more than one mol. deep.

F. L. BROWNE

The sorption of saturated vapors by charcoal. JOHN DRIVER AND JAMES BRIERLEY FIRTH. *J. Chem. Soc.* 121, 2409-14 (1922); cf. C. A. 15, 3920.—Continuing the previous work, the sorption by animal charcoal of Me benzoate, CCl₄, CHCl₃, C₆H₆, Et propionate, Et₂O, CS₂, and C₂H₆ was measured. The time required to reach equil. varied from 14 days for CHCl₃ to 200 days for Me benzoate, and the cc. of liquid sorbed per g. charcoal from 0.4172 for C₂H₆ to 0.6836 for CS₂. The sorption by various carbons of

H₂O, CHCl₃, C₆H₆, and EtOH was measured. The carbons used were lampblack, blood charcoal, sugar charcoal, coconut charcoal from the shell and from the fruit. The time required to reach equil. was least with all liquids for lampblack and greatest for coconut charcoal, while the cc. of liquid sorbed per g. was greatest for lampblack and least for coconut charcoal, the difference being from 2- to 4-fold. Preliminary heating of the carbons greatly decreased the time required to reach equil. and increased the amt. sorbed, the effect being greater the longer the time of preliminary heating and the higher the temp. up to about 900°. At 1000° the effect decreased again, possibly because of conversion of the carbon to a dense, compact form of low sorptive capacity and formation of a more stable cryst. phase. F. L. BROWN

Acceleration of the hydrolysis of mustard gas by alkaline colloidal solutions. R. E. WILSON, E. W. FULLER AND M. C. SCHUR. *J. Am. Chem. Soc.* **44**, 2762-83(1922).—With a soln. contg. 3% of sulfonated corn oil and 2% of Na₂CO₃ the hydrolysis of mustard gas on cloth is completed in 35 min. at 85°. The alk. sulfonated corn oil accelerates only the sp. rate of soln. per unit area of interface, by acting as carrier to transport the mustard gas from the very thin aq. layer through which the gas was diffusing before hydrolysis was complete; it has no tendency to increase the sp. rate of hydrolysis, nor the soly. of the gas in the aq. phase. Alk. soap solns. do not complete the hydrolysis of mustard gas on cloth, because of the formation of a gummy compd. between the hydrolysis product of the gas and the soap, which deposits on the fibers of the cloth. The mechanism of the hydrolysis of PhSO₂Cl is similar in practically every respect to that of mustard gas. H. JERMAIN CREIGHTON

Solubility and rates of hydrolysis of mustard gas in water. R. E. WILSON, E. W. FULLER AND M. C. SCHUR. *J. Am. Chem. Soc.* **44**, 2867-78(1922); cf. preceding abstract.—The hydrolysis of mustard gas in H₂O is a 2-stage reaction, the rate of the 2nd stage depending on that of the 1st. The rate of hydrolysis at 25° in alk. soln. is $dc/dt = 0.304 (M)$, where (M) is the concn. of the gas. In HCl soln. the expression, $dc/dt = 0.304 (M)/(1 + 6.14(Cl^-))$, holds with satisfactory accuracy for a wide range of acid concns. At 25° the soly. of the gas in H₂O is 0.0043 mole per l. H. J. C.

Viscosity of soap solutions. BEVERLY L. CLARK. *Medd. Vetenskapsakad. Nobel Inst.* **6**, No. 1, 9 pp.(1922).—This investigation was undertaken to find how closely the variation of the viscosity of aq. solns. of certain soaps with concn. follows the *viscosity formula of Arrhenius*, $\log(\eta/\eta_0) = \theta c$, and to what extent and between what limits of concn. soap solns. exhibit the abnormality, recognized as peculiar to colloidal solns., of change of viscosity with age. Preliminary expts. showed that if the viscosity measurements were made near the b. p. and in the absence of CO₂ the change of viscosity with age was avoided. For Na stearate at 70° measurements at 3 concns. gave 0.99 ± 0.08 as the mean value of the constant θ and the average deviation of a single detn. from the mean. At 98.4° five concns. gave 0.98 ± 0.03 ; at 98.3° with CO₂ excluded 6 concns. gave 1.08 ± 0.05 . At 18° measurements on the viscosity of Na oleate at 6 concns. gave 1.37 ± 0.04 ; at 98.5° with CO₂ excluded 4 concns. gave 0.85 ± 0.10 . Arrow's data on Na palmitate at 70° and 15 concns. between 0.50 and 0.025 gave 1.14 to 0.04. It is concluded that these soaps all obey the Arrhenius formula within the limits of error of the measurements. D. MACRAE

The flow of liquids under capillary pressure. E. K. RIDEAL. *Phil. Mag.* **44**, 1152-9(1922).—A capillary tube of glass 1.2 m. long and 0.708 mm. av. internal diam. was mounted horizontally in a condenser tube maintained at 20°. The liquid under examn. was then drawn back and forth by suction several times to wet the wall thoroughly, and finally was forced back to a point 15 cm. from the beginning of the capillary, from which point measurements were made of the rate of penetration. The liquids examd. were isobutyl, isopropyl, allyl, Et, and Me alcs., water, water-lit alc. mixts.,

CHCl_3 , C_6H_6 , Et_2O , Me_2CO and AcOH . The rate of advance into the capillary of a liquid under its own force is: $t = (2\eta/\gamma')x^2 - (\delta r^2/\gamma\eta)\log x$ in which t is the time, η the viscosity, γ' the surface tension, x the distance traversed, and δ the d. of the liquid. For relatively large capillaries the penetration coeff. is $\sqrt{\gamma'/2\eta}$. The explt. detn. of the coeff. is shown to agree with calcn. In the case of mixts. the dynamic surface tension and not the static values are probably the governing factors. The reciprocal of the penetration coeff. is proportional to the sq. root of the period of mol. relaxation as defined by Maxwell, and by analogy with reactions in the solid state is probably important in reactions taking place in liquid media. S. C. LIND

Internal friction in solutions of amphoteric electrolytes. GUNNAR HEDESTRAND. *Z. anorg. allgem. Chem.* **124**, 153-84(1922).—A continuation of viscosity measurements of amino acid solns. contg. free acid or base (cf. *C. A.* **16**, 1895). A study of glycocoll (A), alanine (B) and phenylalanine (C) showed that the viscosity of solns. of each passed through a min. This was due to the fact that the friction of the ions is greater than that of the elec. neutral mols. of the ampholyte, and since the concn. of ampholyte ions is then a min. these minima coincided with the isoelec. points of the ampholyte. In terms of H-ion concn. p_H , these min. values for varying concns. and temps., were: A, 0.5 N, 40°, 6.2; 0.5 N, 18°, 5.8; 0.4 N, 40°, 5.8; 0.4 N, 18°, 5.7; B, N, 18°, 6.2; 1 N, 40°, 6.1; 0.5 N, 18°, 6.6; 0.5 N, 40°, 6.6; 0.25 N, 18°, 6.3; C, 0.831 g. per 100 cc., 18°, 5.3. The calcd. isoelec. points gave for p_H : A 6.1, B 6.2, C 5.4. The curves at the min. points were fairly flat and of the same form as the max. of the dissociation curves of ampholytes. The right part of the curves was much steeper than the left, indicating that the friction of the anions was greater than that of the cations. By addn. of neutral salts, the minima were changed. With A, the min. was displaced by NaCl and CaCl_2 toward the alk., by Na_2SO_4 toward the acid. With B, it was displaced by NaCl toward the acid but with KCl and Na_2SO_4 there was no displacement, though the curve became flatter. In all cases the min. of the salt curves was higher than that of the curves without salt. This was caused by the anion and cation reacting to change the min. to the left and right, resp. The decrease in viscosity with B- CaCl_2 was due to the suppression of the dissociation of B-hydrochloride by CaCl_2 . The Cl ion acted similarly with B-NaCl, A-NaCl and A- CaCl_2 . The viscosity of mixts. of A and B was an arithmetic mean of the values of the corresponding individual solns. 1% gelatin soln. had a min. coinciding with the isoelec. point with p_H 4.7. This min. was displaced and slightly increased by neutral salts. To the left of the min. the viscosity increased to a max. with p_H 2.6. With 0.1 N NaCl and 0.1 N Na_2SO_4 the min. was displaced toward the acid, with p_H 4.3 and 4.0, resp. After treatment of powdered gelatin with HCl, HCl- Na_2SO_4 soln. and HCl- CaCl_2 soln., subsequent washing caused the soln. of considerable gelatin, disagreeing with the results of Loeb (cf. *C. A.* **12**, 1974; **13**, 327, 848). C. C. DAVIS

Films. The spreading of liquids and the spreading coefficient. W. D. HARKINS and A. FELDMAN. *J. Am. Chem. Soc.* **44**, 2665-85(1922).—A theoretical paper in which it is shown that the criterion of spreading or non-spreading of liquids may be presented in a very simple way in terms of a simple and thermodynamically detd. coeff., termed the spreading coeff. This coeff. is defined as $S = W_A - W_C$, where W_A is the work of the surface adhesion and W_C the work of the surface cohesion of the liquid. A positive value of S corresponds to spreading, a negative value to non-spreading. Expts. were made with org. liquids on the surface of water and *vice versa*, and with org. liquids and H_2O on the surface of Hg. Almost all org. liquids spread on H_2O , while H_2O spreads on very few org. liquids. The non-spreading of org. liquids on H_2O is brought about by the presence in the org. mol. of Cl, Br, I, =S, =CS, or by Ph groups. Monomol. films are produced on H_2O only when the spreading coeff. has a relatively high value.

These high values seem to occur only when the spreading substance has a polar group in its mols.

H. JERMAIN CREIGHTON

Interfacial tension between gelatin solutions and toluene. S. E. SHEPPARD AND S. S. SWEET. *J. Am. Chem. Soc.* **44**, 2797-2805(1922).—The hypothesis of Sheppard (*C. A.* **15**, 2372) regarding the nature of the *emulsoid colloid state* leads to conclusions which are capable of exptl. verification. In respect to their thermodynamic environment the surface and interfacial tensions are of particular interest. The effect of *H-ion concn.* in the gelatin soln. has been measured (1) by shaking-out expts. where foam and emulsion stabilities were observed, and (2) by allowing the gelatin soln. to drop through toluene and observing the drop-numbers. The stability of gelatin-air foam is greatest at the isoelectric point (about $p_H 5$); and the lowering of the tension by gelatin increases rapidly at this same *H-ion concn.*

JAMES M. BELL

Film method for measuring surface and interfacial tension. A. W. FAHRENWALD. *J. Optical Soc. Am.* **6**, 722-33(1922).—The accuracy is discussed of each of the following methods of measuring surface tension: (1) drop wt., (2) capillary rise, (3) Jaeger, (4) vibrating jet, (5) method measuring the tension required to detach a ring, sphere, or disk from the surface of the liquid, and (6) film method. For oil-water emulsions where the surface tension depends upon the age of the surface, the film method gives the most dependable results. The instrument, which essentially consists of a liquid container, knife edge, automatic balance, pointer and scale, is carefully described. A measurement consists in lowering the knife edge into the liquid, then lowering the liquid until the edge is just about to be detached from the liquid. The liquid container is then lowered very slowly until the pointer is seen to slip back a few divisions which indicates the formation of the film. For most liquids the film lasts several seconds holding the pointer motionless at a given point on the scale. With small corrections, this method can be used for any liquid. By substituting a special frame plate for the knife edge, the tension existing at a liquid-liquid surface can be as readily measured as for the previous liquid-air surface. The instrument is standardized to read directly in dynes per cm. with the value of the surface tension of water, 72.8 dynes per cm., as the basis. The instrument is easily constructed and gives values easily reproducible to 0.1 dyne per cm.

E. F. PERKINS

Solubility. VII. Solubility of salts of aromatic acids. F. EPHRAIM. *Ber.* **55B**, 3472-86(1922); cf. *C. A.* **16**, 3275.—Measurements have been made to det. whether or not the salts are pptd. under comparable conditions of temp. and concn. All expts. have been carried out at room temp. Normal solns. of the Na salts of 73 aromatic acids (carboxylic and sulfonic acids) were added to equi-molar quantities of normal solns. of salts of the following metals: Ba, Sr, Ca, Hg(ic), Mg, Zn, Fe(ous), Mn, Co, Ni, Cu, Cd, Pb and Ag. The results are tabulated and indicate whether a ppt. forms immediately, slowly, or not at all.

H. JERMAIN CREIGHTON

Solubility of iodine pentoxide in sulfuric acid. A. B. LAMB AND A. W. PHILLIPS. *J. Am. Chem. Soc.* **45**, 1084-12(1923).—At 24.77° the initial soly. of I_2O_5 in H_2SO_4 gradually decreases from 50.79 g. per l. in 50% acid to 18.66 g. per l. in 78% acid, and from there on to 106% (29% free SO_3) it steadily rises. Owing to a slow transformation of the solid phase which sets in at 77% H_2SO_4 , with the formation of a less soluble solid substance, the final soly. steadily decreases to a min. of 1.9 g. per l. in 104% acid. There is evidence of a 3rd solid phase in equil. with acids of intermediate concns.

H. JERMAIN CREIGHTON

Measurement of the contraction of volume in mixtures of water and nicotine at different temperatures. MARIA BINGHINOTTO. *Atti inst. Veneto* **79**, 949-63(1920).—Various measurements show that the max. contraction and d. at temps. ranging from 0° to 40° is obtained with solns. contg. between 60 and 70% of nicotine. S. M.

Neutralization of tartaric acid in the presence of metal chlorides. Neutral zones and buffers. L.-J. SIMON. *Compt. rend.* **175**; 887-90(1922).—Fernbach and Hubert (*Ibid* **131**, 293(1900)) introduced the term "buffer" in describing the neutrality to both Me orange (A) and phenolphthalein (B) of a mixt. of NaH_2PO_4 and Na_2HPO_4 . A mixt. of mono- and di-salts of tartaric acid (C) has the same property; but if CaCl_2 be added to K H tartrate, the soln. becomes acid to A, while if added to di-K tartrate, it does not modify the B neutrality; the buffer action is lessened or entirely destroyed. The presence of a chloride of an alkali metal, of Li, Zn, or Mg has no distinct effect, but with CuCl_2 , the acidity of C toward both A and B is increased; FeCl_3 greatly narrows, but does not destroy, the neutral zone. Complex K salts of C with Cu, Zn, and Fe are briefly described.

A. R. ALBRIGHT

Intramolecular ionization. T. M. LOWRY. *Trans. Faraday Soc.*, preprint 1922.—Internally ionized mols. should have a greater elec. moment than those which are neutral throughout. Using *sp. inductive capacity* and *refractive index* as bases, H_2 , O_2 , N_2 , Cl_2 , He , CO , CO_2 , CS_2 , CH_4 , CCl_4 , C_2H_6 , and N_2O were classified as not internally ionized. On the same bases, HCl , CH_3Cl , H_2O , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, NH_3 , SO_2 and CHCl_3 (weak) were classified as ionized. Some of the valence difficulties of the *octet theory* are easily explained if we assume that one of the valences holding an atom of oxygen, for instance, in the mol. is a *covalency* and the other is an *electrovalency*. The O in methylethyl-aniline oxide, in H_2O_2 , and in O_3 are considered to be held in this way. The increasing stability of the Cl acids, with added oxygen, is explained on this basis. In HCl the Cl is negative. In the unstable HOCl the Cl is neutral and O negative. In HClO_2 the Cl carries one positive and each O one negative charge. In HClO_3 and HClO_4 the Cl atoms carry 3 positive and 4 positive charges, resp. This increase of positive charge on the central Cl atom is the cause of the increasing stability. The O acids of S, P, and Si are shown to become more stable as the positive charge on the central atom due to internal ionization increases. In addn., all of the O atoms in an acid radical are held in the same way, if one covalency and one electrovalency are assumed. *Acidity* is due to the repulsive effect of a heavy positive nucleus on the light positive nucleus of H. O increases this effect by withdrawing electrons from the nucleus of the central atom of an O acid. Successive H atoms ionize with increasing difficulty because of the increase in the net negative charge surrounding the positive nucleus. The max. of strength and stability in O acids is attained when 4 O atoms surround the central atom.

F. E. BROWN

Dissociation pressures of certain salt hydrates by the gas-current saturation method. W. C. SCHUMB. *J. Am. Chem. Soc.* **45**, 342-55(1923).—A study of the dissociation of pairs of salt hydrates at 25° gave the following results: BaCl_2 , 2- H_2O , 5.50 mm.; SrCl_2 , 6- H_2O , 8.52 mm.; CuSO_4 , 5-3 H_2O , 7.78 mm.; Na_2SO_4 , 10- H_2O , 19.16 mm.; MgSO_4 , 7-6 H_2O , 12.50 mm.; ZnSO_4 , 7-6 H_2O , 15.34 mm.; FeSO_4 , 7-6 H_2O , 14.56 mm.; CoSO_4 , 7-6 H_2O , 16.58 mm.; NiSO_4 , 7-6 H_2O , 20.69 mm. The *gas-current satn. method* which was employed gives reliable results when due precautions are taken, particularly with regard to the size of the saturator contg. the salt-hydrate mixt., the method of measuring the total internal pressure, the intimate mixing of the 2 solid phases, the rate of flow of the current of air through the app., and the weighing of the water taken up by the air. The objection raised to this method, that sufficient time for the attainment of equil. is not allowed, is without foundation, in view of the results obtained with salt hydrates of low dissociation pressures. The possibility of approaching equil. from both sides is pointed out.

JAMES M. BELL

A method for the static investigation of hydration. MARCEL GUICHARD. *Bull. soc. chim.* **31**, 552-4(1922).—A method and app. are described whereby the H_2O or other liquid (L) in or on a solid, its vapor pressure and the equil. temp. are measured

in a sealed tube *in vacuo* and without weighing. A horizontal reservoir (R) of hard glass contg. the absorbing compd. (C) is connected by a right-angle glass tube to vertical calibrated glass tube (G), the latter contg. L to be absorbed. R after filling is drawn out, evacuated to 0.001 mm. and sealed. If C is hydrated and does not give off L *in vacuo* when cold, a mere increase of its temp. suffices to drive L into G. If C does not hold L *in vacuo* at the ordinary temp., R must be cooled to -80° . If the amt. of L in C is insufficient for the necessary measurements, G must be supplied with L after evacuating the system. To supply this L, G is drawn at its lower end to a capillary and after evacuation is immersed in boiling L, the capillary broken, and sealed after entrance of sufficient L. R is maintained at a definite temp. T by enclosing in an oven, G at another temp. t by a liquid bath, and the connecting tube at a const. temp. by an elec. coil. T represents the equil. of hydration, t indicates the vapor pressure under which this equilibrium exists and the G reading gives at each instant the amt. of L fixed by C. Zero absorption is known by measurements with T high enough and t low enough so that all L is in G. Two corrections are necessary, expansion of L in G due to changes in t , and expansion of L vapor in R due to changes in T . For divariant systems, isotherms are constructed if T is const. and t variable, or isobars if t is const. and T variable, or finally curves of const. concn. if the L level in G is kept const. By heating to 600° , irreversible transformations of C can be investigated. Data obtained by this method are to be published forthwith. C. C. DAVIS

The influence of temperature on two alternative modes of decomposition of formic acid. C. N. HINSHELWOOD, H. HARTLEY AND B. TOPLEY. *Proc. Roy. Soc. (London)* 100A, 575-81 (1922).—By a study of the influence of temp. on 2 simultaneous decompn. reactions, the attempt was made to det. whether increase in *velocity of chem. change* with increase in temp. is due solely to activated mols., having acquired the necessary crit. energy from collision or absorption of quanta, reacting at once, or whether in addn. to this crit. energy they must be in a certain phase. The velocity of decompn. of HCO_2H at 240 – 300° was detd. at which temp. the reactions: (1) $\text{HCO}_2\text{H} \rightarrow \text{CO}_2 + \text{H}_2$ and (2) $\text{HCO}_2\text{H} \rightarrow \text{CO} + \text{H}_2\text{O}$ proceed simultaneously. To this end the pressure increase accompanying the decompn. of vapor was measured, and the gaseous decompn. products were analyzed. The relative velocities of reactions (1) and (2) varied considerably with nature of the glass surface and even differed in 2 bulbs of similar glass and the same area and vol. Calling K_{CO_2} and K_{CO} the velocity consts. for reactions (1) and (2) resp., the mean temp. coeffs. for a 10° rise (K_{t+10}/K_t) were found to be: $K_{\text{CO}} 1.82$ and $K_{\text{CO}_2} 1.35$. Since according to Haber (cf. C. A. 4, 1261) the ratio CO_2/CO in water-gas is 6.9 at 300° and 3.7 at 400° , the increased production of CO_2 at higher temps. might be due to a secondary interaction of CO and H_2O . But this secondary reaction was found to be negligible even at 350° . In Jena glass there was always less H produced than CO_2 , indicating that the reaction: $2\text{HCO}_2\text{H} \rightarrow \text{HCHO} + \text{CO}_2 + \text{H}_2\text{O}$ had occurred to a slight extent (cf. Sabatier and Mailhe, C. A. 6, 619). The presence of H_2O initially did not influence the reaction appreciably. To disprove that the higher temp. coeff. of (1) might be due to its taking place in the homogeneous phase, the relation between the velocity of decompn. and the area of the glass surface was detd. The reaction velocity should be much less dependent on the area/vol. ratio of the glass than at lower temps. Actually the velocity increased not merely in proportion to the area of the walls of the vessel, but even more rapidly. At 294° reaction (1) was still as largely influenced by the surface of the glass as (2). Calcn. of the crit. increments by the formula $d(\log k)/dt = E/(RT^2)$ gave for (1) in cal. per mol.: $E_{\text{CO}_2} = 28,000$ and $E_{\text{CO}} = 16,000$. Since the no. of mols. activated is proportional to $e^{-28,000/(RT)}$ and $e^{-16,000/(RT)}$, approx. 10^6 mols. should yield CO for 1 yielding CO_2 . Since the rates are of the same order, a phase restriction may be present. It is suggested that the HCO_2H mol. is adsorbed by the resid-

ual affinity of the $=\text{CO}$ group, and that with a sufficiently activated mol., a violent collision between $-\text{H}$ and $-\text{OH}$ occurs and a H mol. is split off. Though the requisite activation may occur but rarely, a high % of collisions of the activated mols. may still result in this decompn. But for H_2O to be eliminated and CO left, a high activation is not necessary, perhaps because the removal of an $-\text{OH}$ group is a less profound change than the fission of H and O . Few of the activated mols. decomp; however, because this can occur only when the forces holding $-\text{OH}$ and $-\text{H}$ to the C are simultaneously weak enough to allow uncoupling of the mol.

C. C. DAVIS

Absorption of carbon monoxide by cuprous ammonium carbonate and formate solutions. A. T. LARSON AND C. S. TEITSWORTH. *J. Am. Chem. Soc.* **44**, 2878–85 (1922).—Solns. of cuprous ammonium carbonate, $\text{Cu}_2(\text{NH}_4)_2\text{CO}_3$, and of cuprous ammonium formate at equiv. concns. have the same absorptive capacity for CO under the same conditions of temp. and pressure of CO . At 0° there is the formation of a complex contg. 1 mol. of CO per mol. of Cu , the complex being largely broken up when the temp. is raised to 60° . The carbonate solns. are much less stable than the formate solns., Cu being deposited from the former at 60° . The formate solns. are therefore preferable to the carbonate solns.

JAMES M. BELL

Velocity of absorption of carbonic acid by ammoniacal solutions. PAUL RIOU. *Compt. rend.* **175**, 472–4 (1922).—The influence of the concn. of $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 and of temp. upon the velocity of absorption of CO_2 in the absence of Na salts has been studied. When the velocity of absorption was plotted against either concn. or temp. the complete curves could not be obtained, with the app. used, for $(\text{NH}_4)_2\text{CO}_3$ soln., but with the addn. of $(\text{NH}_4)\text{HCO}_3$ all the curves pass through a max.

E. P. WIGHTMAN

Equilibria between the acido- and aquo-iridium pentammines. A. B. LAMB AND L. T. FAIRHALL. *J. Am. Chem. Soc.* **45**, 378–95 (1923).—The reversible transformations of the acido- and aquo-iridium pentammine chlorides, bromides, iodides and nitrates were investigated at 95° (and in the case of the bromo amines also at 80°) by means of elec. cond. measurements and the equil. concns. established from both sides were detd. by direct analysis of chilled samples. A special form of *quartz cond. cell* for use at this temp. is described and a modified method for the *exact analysis of minute amts. of halides* is reported. The transformations in both directions follow the course of a monomol. reaction and their velocity const. have the same relative magnitudes as the corresponding const. of the Co amines. The values for the equil. concns. agree substantially with those calcd. from the velocity measurements and are similar to those of the corresponding Co amines. The equil. const. in the case of the aquo- and bromo-pentammine iridium bromides was computed from the empirical equation $[\text{C}_\text{B} \times \text{C}_\text{B}^-]^{0.46} / \text{C}_\text{B} = K_2$ and found to give good agreement in the values of K_2 . A comparison of similar data for the Ir amines and Co amines indicates that while the exchange of the central Co atom for an Ir atom has produced a general shift in the velocity and equil. const., it has produced no relative displacements among the amines studied.

L. T. F.

Equilibrium of the reaction between metallic silver, cupric chloride in aqueous solution, and solid cuprous and silver chlorides. GRAHAM EDGAR AND L. S. CANNON. *J. Am. Chem. Soc.* **44**, 2842–9 (1922).—The equil. of the reaction $\text{CuCl} + \text{AgCl} \rightleftharpoons \text{Cu}^{++} + \text{Cl}^-_{-2} \cdot \text{aq} + \text{Ag}$ has been measured at 25° and 40° in the presence of varying quantities of HCl , and the equil. const., the increases in free energy and the heat content of the system have been calcd.

H. JERMAIN CREIGHTON

The partition coefficient and the determination of organic acids by extraction. JOH. PINNOW. *Z. Nahr. Genussm.* **44**, 204–9 (1922); cf. *C. A.* **9**, 2732.—The fact that AcOH and HCOOH form double mols. in Et_2O explains the irregularities observed by

Fresenius and Grünhut in the detn. of the partition coeff. of HCOOH (cf. *C. A.* **16**, 985). Tables are given showing the distribution of these acids between Et_2O and water at 15° and HCOOH at 26.3° . The sugar content does not influence the extn. of succinic acid from water.

D. B. DILL

Is a true monomolecular action possible? T. M. LOWRY. *Trans. Faraday Soc.* **17**, 596-7(1922).—The fact that the sp. reaction rate of a unimol. reaction is independent of the concn. (and hence of the frequency of mol. collision) constitutes one of the strongest arguments in favor of the radiation hypothesis. L. suggests that perhaps there are no true unimol. reactions, with the exception of radioactive decompn. He cites the work of Baker which shows that most gas dissociations which are ordinarily considered to be unimol. reactions require the presence of traces of a 2nd substance such as water or other catalyst. L. and also Meyer have shown that catalysts are necessary even for tautomeric transformations.

FARRINGTON DANIELS

Velocity law for monomolecular reactions. J. A. CHRISTIANSEN. *Z. physik. Chem.* **103**, 91-8(1922).—A mathematical paper. On the assumption that only the mols. in a certain "quanta-state" (designated by m , while the normal state is represented by n) are capable of reacting, it is shown that the velocity const. of a monomol. reaction is given by the expression, $k = (p_m/p_n)e^{-(\epsilon_m - \epsilon_n)/RT} \cdot \nu / (1 - e^{-h\nu/RT})$ where p_m and p_n are the *a priori* probabilities of the m and n states, ϵ_m and ϵ_n the corresponding energies reckoned from an arbitrary null-point, and the other quantities have their usual significance. It is also shown that Dushman's equation (cf. *C. A.* **15**, 1443) and Herzfeld's equation (cf. *C. A.* **16**, 1440, 3418) are special cases of the equation given above. Dushman's formula has been combined with Ribaud's expression for the inner mol. "vaporization-coeff." (cf. *C. A.* **16**, 2792).

H. JERMAIN CREIGHTON

Study of catalysis in the preparation of acetal. H. ADKINS AND B. H. NISSEN. *J. Am. Chem. Soc.* **44**, 2749-55(1922).—Ca, Li, Mg, Ce, NH_4 , Mn and Zn chlorides, $\text{Ca}(\text{NO}_3)_2$, CaBr_2 , CuSO_4 , NaF and LiI act as true catalysts, and not merely as dehydrating agents, in the prepn. of acetal from acetaldehyde and alc. A yield of about 65% has been obtained on a moderately large scale in the method developed. The products of the reaction, $\text{CH}_3\text{CHO} + 2\text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2 + \text{H}_2\text{O}$, are in equil. (under the conditions employed) when 76% of the theoretical amt. of acetal is present. The vapor pressure over a large range of temp. and the soly. of acetal in alc. and H_2O have been detd.

H. JERMAIN CREIGHTON

Preparation of active nickel catalysts. ANDRÉ BROCHET. *Compt. rend.* **175**, 816-9(1922).—The study of several hundreds of prepn. of Ni catalysts leads to the conclusion that products of the most uniform character, but not necessarily the greatest activity, are to be prepd. by heating to const. wt. com. "hydrated nickel oxide" contg. a considerable proportion of carbonate, and reducing the oxide thus formed at 800° during 48 hrs. with electrolytic H; the pyrophoric properties of this prepn. are destroyed by passing CO_2 over it while still hot, and cooling in absence of air. $(\text{HCO}_2)_2\text{Ni}$ or $(\text{CO}_2)_2\text{Ni}$ may be used in place of the basic carbonate. Cf. U. S. patent 1,001,279; *C. A.* **5**, 3791. Some properties of active nickel used as a catalyst. *Ibid* 1073-5.—Further discussion.

A. R. ALBRIGHT

Colloids in catalytic hydrogenation. E. F. ARMSTRONG AND T. P. HILDITCH. *Brit. Assoc. Advancement Sci.*; 4th Rept. **1922**, 327-46.—"The activity of catalysts employed in the hydrogenation of gaseous or liquid org. compds. is connected with the colloidal state to the extent that it is largely dependent upon the surface at which the interaction takes place, although catalysts which are definitely colloidal sols are actually less energetic in their action than various other types. The most efficient agents are those possessing a capillary or fibrous structure exposing a max. surface per unit mass; sometimes the metal itself may be obtained in this form (e. g., spongy Pt or Pt black)

but more frequently it is found necessary to deposit the catalyst in the form of a ppt. of one of its compds. upon an inert material (a "catalyst support") of a permanently porous structure such as pumice, certain forms of charcoal, asbestos, diatomaceous earth, or similar substances." Apart from sp. chem. changes, the accessibility of the catalyst surface to H and the org. compd. is the chief general factor in hydrogenation reactions. These are (in increasing order of difficulty): satn. of ethylenic and acetylenic linkages; reduction of oxides of N to NH_3 ; reduction of CO and CO_2 to CH_4 ; reduction of aldehydes and ketones to corresponding alcs. or hydrocarbons; reduction of nitro compds., amides, nitriles and oximes to amino compds.; hydrogenation of the benzenoid nucleus; hydrogenation of heterocyclic (N) nucleus. This report excludes synthesis of NH_3 , being limited to org. compds. The catalysts are considered under the following groups: Colloidal sols (Pd and Pt); nonsupported finely divided metals (Pd, Pt, Ni, Cu); supported finely divided metals (Pd, Ni). Then follow discussions of catalytic dehydrogenation, essential conditions of the catalytic surface (extent, protective action of supports, catalyst poisons and stimulants); the mechanism of hydrogenation (phys. theories, intermediate chem. compds., e. g., metal hydrides, oxyhydrides, "nickel sub-oxide," unstable metallo-org. compds. associated with metal-H complex). An extensive bibliography is appended.

JEROME ALEXANDER

"Normal temperature" for chemical measuring instruments and hydrometers. W. DZIOBEK. *Z. angew. Chem.* **35**, 665-6(1922).—The adoption of 20° as a standard temp. for calibrating measuring vessels and hydrometers is welcomed, and the advantages and obstacles in the way of complete adoption are considered. W. C. EBAUGH

Comparison of the normal boiling temperatures of undesicated sulfur as measured by the dynamic and the static methods. ALAN W. C. MENZIES. *J. Am. Chem. Soc.* **45**, 327-31(1923).—Several cases are cited where freshly formed liquid and gas phases show abnormal behavior in respect to b. ps. and vapor pressures. Such a substance would give different b. ps. by the static method and by the dynamic method. For S the results are negative, the b. p. by the 2 methods being the same within the exptl. error.

JAMES M. BELL

Normal acids of Berthelot and the theory of ions. F. BOURION. *Compt. rend.* **176**, 95-8(1923).—Calcs. of the heat produced by mixing 1 mol. of a weak acid with a strong base in sufficient quantity for complete neutralization, are made in terms of V the final vol., K the dissoc. const. of the acid, and q the heat of dissoc. of the acid. These values are not far from those calcd. by proportion, i. e., by multiplying the mol. heat of neutralization by the no. of mols. of base. Similar calcs. where the salt hydrolyzes show that the first addns. of base to an acid produce more heat than later addns. of equal amt.

JAMES M. BELL

Thermal decomposition of phosgene. J. A. CHRISTIANSEN. *Z. physik. Chem.* **103**, 99-138(1922).—A study of the kinetics of the decompn. of COCl_2 . Between 705° and 745° abs. the velocity (h) of the decompn. of COCl_2 is given by the expression, $h = k\sqrt{C_{\text{Cl}_2}}[C_{\text{COCl}_2} - (C_{\text{CO}} \cdot C_{\text{Cl}_2}/K)]$, where k is a const. and K is the equil. const. of the decompn. of COCl_2 . This equation holds, however, only if the concns. of CO, Cl_2 and COCl_2 are of the same order of magnitude (10^{-3} to 10^{-4} mol. per l.), or if sufficient time has elapsed from the beginning of the reaction. The deviation at the beginning is always positive, i. e., the measured velocity is always greater than that calcd. according to the equation. The cause of this may be due to some exptl. error. The relative glass-surface (surface/vol.) has little or no influence on the velocity. Neither is the velocity influenced by air, if the concn. of Cl and CO is considerable. On the assumption that the expression for the velocity of the decompn. does not change with temp., $\log k = (-11420/T) + 15.154$, between 685° and 782° . The results of previous expts. are discussed.

II. JERMAIN CREIGHTON

Energetics of sucrose inversion. THOMAS MORAN AND H. A. TAYLOR. *J. Am. Chem. Soc.* **44**, 2886-92(1922).—Moran and Lewis (*C. A.* **16**, 4116) have indicated equations by which the inversion of sucrose may be expressed. In the estn. of the sum of the *crit. increments* of sucrose dihydrate and unhydrated H ions as 35,000 cals., the assumption was made that the p. d. on the normal H electrode is directly proportional to the abs. temp. Potentiometer measurements with AcOH indicate that the assumption is justified. The theory of Lewis (*C. A.* **12**, 2470) connecting crit. increment and the frequency characteristic of the substance which brings about the reaction predicts a band at wave length 0.815μ . As both sucrose and fructose exhibit such a band at 0.875μ while for glucose there is no band in this region, it appears probable that the fructose portion of the sucrose mol. must be the reactive part. The cause of the discrepancy of 2400 cals. between the calcd. 35,000 cals. (corresponding to frequency 0.815μ) and the observed 32,600 cals. (corresponding to frequency 0.875μ) is ascribed to the attachment of 2 mols. of water to the ethylene oxygen of the fructose portion of the sucrose mol. The series of structural changes probably involved in the inversion process is discussed in some detail.

JAMES M. BELL

System ammonium sulfate-beryllium sulfate-water at 25°. H. T. S. BRITTON. *J. Chem. Soc.* **121**, 2612-6(1922); cf. Britton and Allmand, *C. A.* **16**, 33.—Since attempts to prep. BeSO_4 by dissolving the hydroxide, pptd. by NH_4OH , in H_2SO_4 had proved unsuccessful on account of the formation of the double sulfate from ammonia retained by the ppt., the present work was undertaken to find how much NH_3 is retained by $\text{Be}(\text{OH})_2$ and to investigate the ternary system $(\text{NH}_4)_2\text{SO}_4\text{--BeSO}_4\text{--H}_2\text{O}$ at 25°. $\text{Be}(\text{OH})_2$ pptd. in the cold from H_2SO_4 soln. and dried for 50 hrs. at 100° had the following compn. expressed in molal proportions: BeO , 1.00; H_2O , 1.111; BeSO_4 , 0.043; $(\text{NH}_4)_2\text{SO}_4$, 0.614. When pptd. from H_2O soln. and dried for 10 days at 15° it had the compn.: BeO , 1.00; H_2O , 3.112; BeSO_4 , 0.039; $(\text{NH}_4)_2\text{SO}_4$, 0.444. If the ppt. is finely ground and boiled with H_2O the $(\text{NH}_4)_2\text{SO}_4$ is completely extd. but it is very difficult to remove the last traces of BeSO_4 . The phase diagram for the ternary system is given. The solid phases crystg. at 25° are $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, $\text{BeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{SO}_4$.

D. MACRAE

Activity coefficient of hydrochloric acid in aqueous salt solutions. H. S. HARNED AND N. J. BRUMBAUGH. *J. Am. Chem. Soc.* **44**, 2729-48(1922).—Measurements of cells of the following types were made: $\text{H}_2 | \text{MCl}_2 \text{ in HCl } (0.1 \text{ } M) | \text{HgCl} | \text{Hg}$ at 18°, 25° and 30°; $\text{H}_2 | \text{MCl}_2 \text{ in HCl } (0.1 \text{ } M) | \text{satd. KCl} | \text{HgCl} | \text{Hg}$ at 25° where M denotes Ba, Sr or Ca; $\text{H}_2 | \text{KCl } (c_1) \text{ in HCl } (c_2) | \text{AgCl} | \text{Ag}$, and $\text{H}_2 | \text{KCl } (c) \text{ in HCl } (c_1) | \text{HgCl} | \text{Hg}$ contg. acid at 0.01 *M* and 0.001 *M* at 18°, 25° and 30°. From the data the decrease in free energy, the heat content decrease of the cell reaction, the changes in partial molal free energy, and the heat content of HCl in the mixts. have been computed. The mean activity coeffs. of HCl in solns of chlorides of K, Na, Li, Ca, Sr, and Ba have been computed and have been found to accord with the formula $\log f_{\text{HCl}} = \alpha'c_1 - \beta'\mu^{m'} + \alpha''(\mu - c_1)$ for concns. from 0.01 to 1 *M* in acid. At lower concns. it is necessary to add a term to the formula, $\gamma'[(\mu - c_1)c_1]$, where c_1 is the concn., μ is the ionic strength and the other letters are consts. This effect for low concns. is probably due to an increase in activity of the H ion. Further conclusions are that in solns. of strong bivalent chlorides at the same concn. and temp. the Cl ion has the same activity, and that the activity of the Cl ion in uni-univalent chloride solns. is greater than in bivalent chloride solns. of the same ionic strength.

JAMES M. BELL

Surface properties of mercury: voltaic character, surface tension, photoelectric effect. ELIGIO PERUCCA. *Compt. rend.* **175**, 519-22(1922).—The Volta effect between Hg and a plate of Pt was measured in vacuum, and in air, N_2 , CO_2 and H_2 at low pressures, by means of the variable condenser method. In vacuum the voltaic character of the

Hg does not vary sensibly with time. In the gases, however, the Hg is at the start electro-negative by 0.3 v., then rapidly becomes electropositive, attaining asymptotically the value which it had in vacuum. The time necessary to attain the limit increases regularly with the pressure of the gas, of the order of 1 min. for a pressure of 0.1 mm. and of 10 min. for a pressure of 10 mm. At equal pressures the time is least for H_2 and greatest for CO_2 . Other expts. were made simultaneously to det. the surface tension of the Hg under the various conditions. In vacuum there is very little change in the surface tension. In gases, however, the surface tension varies with time parallel to the voltage variation, and also increases with the pressure of the gas. The relation between voltage and surface tension is as yet only qual., because the scales chosen for comparison were arbitrary. Nevertheless, the relation is truly splendid and is a new confirmation of the soundness of the anticontact theory and of Frankel's theory. E. P. WIGHTMAN

New evidence regarding the interpretation of critical potentials in hydrogen. P. S. OLMSHEAD. *Phys. Rev.* 20, 613-30.—O.'s synopsis is as follows: In an ionization tube of the Lenard type, a close grid of W wires was introduced between the filament and the gauze in front of the plate. When this grid was electrically heated to incandescence the proportion of atoms was greatly increased by dissociation of the mols. Effects due to radiation were distinguished from effects of ionization by comparing the electron currents to a disk electrode with those to a wire which because of its small area was relatively insensitive to effects of radiation. Six crit. potentials between 10 and 16 v. were observed and measured with reference to the strongest break, assumed to occur at 16.0 v. Each break point was located at the intersection of 2 tangents; hence the relative values are probably accurate to 2 or 3%. Purified electrolytic H was used. Exptl. interpretation of the breaks, which agree in general with the previous theoretical interpretation based on the quantum theory, is as follows: radiation from the atom at 10.1 and at 12.2 v., corresponding to the first terms of the Lyman series; ionization of the mol. at 11.5 and of the atom at 13.6 v.; dissociation of the mol. and radiation at 12.9 v.; finally, dissociation of the mol. and ionization of one of its parts at 16.0 v. The energy required for dissociation of the mol. is therefore equiv. to about 2.8 v.

JAMES M. BELL

The electrical conduction in metallic aggregates. W. ESMARCH. *Jahrb. Radioakt. Elektronik* 19, 141-61 (1922).—E. has continued the researches begun by Benedicks (*Jahrb. Radioakt. Elektronik* 13, 351 (1916); 14, 470 (1917); 17, 292) on methods of artificially imitating metallic aggregates with reference to their elec. cond. From measurements on the circular model the following results were obtained: (a) The cond. is not a linear function of the compn. in vol. %; (b) the deviation from the linear relation is greater, the more the ratio of the conds. of the constituents differ from unity; (c) the observed values for the cond. are lower than those calcd. from the linear relation. From measurements on the checker-board model of Guertner (*Jahrb. Radioakt. Elektronik* 5, 17 (1908); 17, 276 and 298 (1921)), it was concluded that the method of calcg. resistance put forth by Lichteneker (*Jahrb. Radioakt. Elektronik* 14, 466 (1917); *Physik. Z.* 10, 1005 (1909)), holds only for small values of K where K is the ratio of the thickness of one plate constituent to that of the other. J. A. ARMQUIST

Theory of electrocapillarity. I. Electrocapillary phenomena in non-aqueous solvents. A. FRUMKIN. *Z. physik. Chem.* 103, 43-54 (1922).—Electrocapillary curves have been detd. for the following solns.: 0.1 N and 1.0 N NH_4NO_3 , 1.0 N $NaBr$, and 1.0 N NaI in $MeOH$; 0.2 N NH_4NO_3 , 1.0 N $LiCl$, and 1.0 N NaI in $EtOH + H_2O$; 0.9 N $LiNO_3$, 0.5 N $LiCl$, and 1.0 N NH_4CNS in Me_2CO ; 1.0 N NH_4CNS , and 1.6 N NaI in C_2H_5N . The curves obtained indicate that the activity of the anions has the same values in the above solvents as in H_2O . The max. of the curves for these solns., compared with aq. solns. of the same compn., corresponds to a smaller cathodic polar-

ization. II. *Ibid* 55-70.—The whole region of electrocapillary phenomena is governed by the differential equation, $d\gamma = e\phi - \Sigma \Gamma_i d\mu_i$, where γ is the tension of the surface of sepn., ϕ is the p. d. at the junction, soln./Hg, e is the density of the charge on the Hg surface, and Γ_i and μ_i are, resp., the surface density and the thermodynamic potential of the ions (anions or cations) of the soln. The Lippmann-Helmholtz differential equation, $d\gamma/d\phi = E$, holds for solns. with both normal and abnormal electrocapillary curves. Values of ϕ_{max} were obtained by means of measurements with the chain, $\text{Hg} \mid N \text{ KCl, Hg}_2\text{Cl}_2 \mid \text{Soln.} \mid$ drop electrode, in which different solns. were employed. The results show that the potential of a drop electrode always coincides with the max. of the corresponding electrocapillary curve. The potential between Hg on the one hand, and H_2O , MeOH , EtOH , and Me_2CO on the other, persists, provided the surface layer contains neither ions nor adsorbed mols. of a solute. The results of the whole investigation indicate the necessity of modifying the accepted conception of soln. tension, by which at present are designated both thermodynamic soln. tension and capillary-elec. soln. tension. These two quantities are very different. Thus, the thermodynamic soln. tension of Hg in EtOH is approx. $10^{6.1/0.02}$, or 3000 times smaller than in H_2O ; while the capillary-elec. soln. tension of Hg in EtOH is $10^{6.2-6.4/0.02}$ or 3000 times greater than in H_2O .

H. JERMAIN CREIGHTON

Electrocapillary curves in non-aqueous solutions. W. WILD. *Z. physik. Chem.* 103, 1-38(1922); cf. Baur C. A. 17, 17.—Electrocapillary curves have been detd. for solns. of the electrolytes (MS) KCl , KNO_3 , $\text{Hg}_2(\text{NO}_3)_2$ and HNO_3 in the following solvents: AmOH , $\text{C}_6\text{H}_5\text{OH}$, furfural, $\text{C}_6\text{H}_5\text{NH}_2$, CHCl_3 , PrOH , iso-BuOH , Et_2O and EtOAc . The abs. potentials, π_1 and π_2 , of the chain $M \begin{array}{c} \text{MS} \\ \text{phase I} \end{array} \begin{array}{c} \text{MS} \\ \text{phase II} \end{array} M$, formed by shaking

$\pi_1 \quad \pi_3 \quad \pi_2$

an aq. soln. of MS with a second non-aq. solvent until distribution equil. was attained, have been deduced from the electrocapillary curves with an accuracy of 5 to 10 milliv. The results are unambiguous and show that in all cases $\pi_1 = \pi_2$. Since the phase potential, π_3 , is equal to $\pi_1 + \pi_2$, it follows that π_3 is either zero or less than 5 to 10 millivolts. While that conclusion undoubtedly holds for all solvents, it is by no means certain that it also holds for all ions.

H. JERMAIN CREIGHTON

Phase-potentials. E. BAUR. *Z. physik. Chem.* 103, 39-42(1922); cf. preceding abstr.—The p. d., π_3 , at the liquid-liquid junction in the chain $M \begin{array}{c} \text{MS} \\ \text{phase I} \end{array} \begin{array}{c} \text{MS} \\ \text{phase II} \end{array} M$

$\pi_1 \quad \pi_3 \quad \pi_2$

may be due to (1) the effect of selective partition of ions between the 2 phases, (2) adsorption of ions, or (3) to a combination of (1) and (2). Wild's results are discussed, and it is pointed out they not only show that within the limits of exptl. error the phase potential due to cause (1) is zero, but they substantiate B.'s opinion that the phase potential arises from cause (2).

H. JERMAIN CREIGHTON

The variation with temperature of the dielectric constant and the density for certain liquids. M. JEZEWSKI. *J. phys. radium* 3, 293-308(1922).—J. has measured the dielec. consts. and the ds. for nitrobenzene, aniline, glycerol and water, over a wide temp. range. The dielec. consts. were measured by the method of resonance in a high-frequency circuit. A discussion of errors in this method is given. The d. was obtained by weighing a quartz sinker in the liquids. Formulas are given for the change of d. with temp. The results are used to test Debye's equation: $(\epsilon - 1)/(\epsilon + 2) (1/\rho) T = a + b/T$, where ϵ is the dielec. const. and ρ the d. Values for a and b are obtained, but a is negative except for aniline. The equation, then, is not entirely verified.

FARRINGTON DANIELS

Orientation of molecules in a magnetic field, MARSHALL HOLMES. *Nature* 110,

635(1922).—A parallel pencil of X-rays, directed through a small cell contg. BaI_2 placed between the poles of a large electromagnet, was allowed to fall on a photographic plate. The disk appearing after development of the plate was about 10% greater in diam. for exposures during which the magnet was excited than when it was not excited. This result is taken to indicate that orientation of mols. in a magnetic field does take place.

D. MACRAE

Residual affinity and coördination (MORGAN, SMITH) 6. Missing element of atomic number 72 (COSTER, HEVEY) 3. Spatial progress of photochemical reactions in jellies (BENRATH, SCHAFFGANSZ) 3.

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3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Missing element of atomic number 72. D. COSTER AND G. HEVESY. *Nature* 111, 79(1923).—Dauvillier's (*C. A.* 16, 2638) discovery of lines belonging to the X-ray spectrum of this element (which Urbain (*C. A.* 16, 3804) has identified with the supposed rare earth celtium) is questioned on the following grounds: (1) The two lines discovered by D. are extremely faint and differ by about 4×10^{-11} cm. in wave length from the values calcd. by interpolation in the measurements of Hjalmar and Coster. (2) According to the Bohr theory 72 should not be a rare earth but a homolog of Zr. (3) General views based on the periodic system lead one to expect a Zr homolog rather than a rare earth in this space. C. and D. have studied the X-ray spectrum of Zr prepns., and find 6 lines which must be ascribed to element 72 (Siegbahn's L, α_1 , α_2 , β_1 , β_2 , and γ). The values of λ are 1565.5, 1570, 1371.4, 1323.7, 1350.2, 1177 X.u., which agree with the interpolated values. In a Norwegian Zr mineral the new element is estd. to be present to the extent of 1%. The name *hafnium* (for Copenhagen) is proposed for element 72.

NORRIS F. HALL

Attempts to separate the isotopes of chlorine by adsorption in charcoal. JITSU-SABURO SAMESHIMA, KAZUO AIHARA AND TOSHIKI SHIRAI. *J. Chem. Soc. Japan* 43, 761-6(1922).—In an attempt to sep. isotopes of Cl, HCl gas was used instead of Cl. The gas was obtained by dropping pure H_2SO_4 on HCl, dried through H_2SO_4 , $CaCl_2$ and passed over charcoal. HCl, H_2SO_4 and $CaCl_2$ used did not contain any other halogens. Bamboo charcoal was used. The app. was so arranged that HCl gas was first adsorbed by charcoal and then driven out into other charcoal by heating the first up to 110° . Then the first charcoal was again heated up to 220° and the gas evolved was adsorbed by 3rd sets of charcoal. The portion coming out between 110° and 150° was discarded. After several repetitions, these two sets of HCl were absorbed by NaOH prepd. by metallic Na and steam. The NaCl formed was analyzed according to Richard's method. The at. wt. of Cl obtained from HCl driven out by heating up to 110° was 35.4612 ($A_g = 107.88$) and that of Cl from HCl at $150-220^\circ$ was 35.4588. Since this difference is within exptl. errors, S. A. and S. concluded that isotopes of Cl cannot be sep'd. by charcoal.

S. T.

β -Ray tracks. W. BOTHE. *Z. Physik* 12, 117-27(1922); cf. *C. A.* 17, 675.—A more detailed account.

NORRIS F. HALL

Theory of the scattering of β -rays. GREGOR WENTZEL. *Ann. Physik* 69, 335-68 (1922).—Full mathematical details of the theory outlined in *C. A.* 17, 674. N. F. H.

The adsorption of radium B and radium C by ferric hydroxide. J. A. CRANSTON AND ROBERT HUTTON. *J. Chem. Soc.* 121, 2843-9(1922).— $Fe(OH)_3$ adsorbs Ra B and Ra C in proportions varying with the acidity of the solution in a manner similar to that for Th B and Th C* (*C. A.* 16, 1042). The ratio of Ra B to Ra C adsorbed at a definite acidity is different from the ratio of their isotopes, Th B and Th C, adsorbed at the same acidity. In 2 expts. on the simultaneous adsorption of the four elements, the ratios Ra B/Ra C adsorbed were 0.18 and 0.2, resp., and of Th B/Th C adsorbed, 4.1 and 4.8. It would thus appear that a partial sepn. of isotopes has been effected. This is explained on the colloidal theory already put forward. C members formed from colloidal B members are adsorbed owing to the predominating influence of the remainder of the B members. Hence the adsorption of the C members is in greater proportion for the Ra series because the period of Ra B is less than that of Th B.

MARIE FARNSWORTH

The black quartz of the radium-bearing mine of Viaris (Portugal). A. BENSUAUDE AND G. COSTANZO. *J. phys. radium* 3, 384-8(1922).—It was thought that the existence

of black layers in this quartz was due to the action of Ra in autunite incrustations on the surface of the quartz. Expt. showed, however, that the clear layers of this quartz, like other clear quartz, will readily darken on exposure to penetrating, (β and γ) rays; hence the natural dark color of the other layers is not due to radiation, but to some pigment present when the layers were formed, long before the radioactive material was deposited in the vicinity.

NORRIS F. HALL

Radioactivity of (a spring at) l'Echaillon in Maurienne. J. CLUZET AND A. CHEVALIER. *Compt. rend.* 175, 1163-5(1922).—The sediments emit Th Em, the dissolved gases contain a little Ra Em, and the undissolved gases Ra Em (but the method used would not have shown Th Em if present). The air in the neighborhood is highly ionized. This is the only natural water in France contg. Th Em suitable for therapeutic use.

NORRIS F. HALL

Radioactivity of the springs of the Herculean Baths in Roumania. P. LOISEL AND MICHAILESCO. *Compt. rend.* 175, 1054-6(1922); cf. *C. A.* 16, 689; 17, 491.—The emanation content of the waters from the different thermal springs was detd. The results varied not only from one spring to another but also from day to day. Some of the springs showed a marked radioactivity, the emanation content ranging from 0.19 to 0.73 milli-microcuries per l.

G. FAILLA

Excitation of the atom to light emission by electron impact. V. Behavior of combination lines. R. SELIGER. *Z. Physik* 11, 197-200(1922); cf. *C. A.* 16, 871, 1906.—In Hg vapor a steady condition of pure glow discharge was obtained at about 750 v. and 2 milli-amp. The intensity of the 2 pairs of lines, 2875-4916 and 2652-4339, was studied photometrically with reference to the pressure and it was shown that the pairs behave quite differently. The probability of passage from one stationary state to another depends upon the elec. field and upon the distribution of ion density in a different way for each spectrum line. It may be possible to gain quant. knowledge of the distribution of ion density from the correspondence principle.

F. O. A. ANDEREGG

Low voltage arcs. I. Hydrogen, nitrogen and iodine. O. S. DUFFENBACK. *Phys. Rev.* 20, 665-87(1922).—Current-voltage curves are given for 2-electrode tubes contg. pure gases. The breaking potentials are at the ionization potentials. The striking voltages are somewhat higher, increasing with increasing pressure and with increasing temp. of the hot cathode. The arc will hold at 10 v., under very favorable conditions, in H dissoed. by a hot W cylinder. In at. I a similar effect was observed. N showed no appreciable dissociation. The crit. potentials check the best previous results within 0.2 v. *Elec. furnace spectra* were studied at 2500°. In H there were no bands, only the series lines, as low as 10.6 v. In N a "flare" was produced showing both positive and negative bands; the flare was supposed to be caused by active N. At 70 v. the lines 5006 and 5003 Å. appeared, and at 90 v. only 2 more, 5680 and 5667. The positive bands are assigned to the neutral mol., the negative bands to the ionized mol. and the lines to the atom. The W spectrum was also produced and the black deposit forming on the walls in N was supposed to be a W nitride. On striking the arc in I the arc lines were found and the enhanced lines at higher potentials, but no bands. *New negative bands of N* were found at 5075, 5018 and 4961 Å.

F. O. ANDEREGG

The present status of the shot-effect problem. C. A. HARTMANN. *Physik. Z.* 23, 436-8(1922).—A review. The shot effect problem deals with the excitation of an elec. oscillator by means of a discharge produced by the unordered transfer of numerous carriers of electricity all alike.

F. O. ANDEREGG

A new method for the determination of e/m . H. BUSCH. *Physik. Z.* 23, 438-41(1922).—The method consists in measuring the discharge potential in a Braun tube simultaneously with the magnetic field which, applied longitudinally, will focus the bundle of diverging cathode rays. A preliminary value of 1.768×10^{-1} e.m.u. is ob-

tained for e/m . The method should be capable of further refinement to yield results within 0.1%. F. O. ANDEREGG

Secondary cathode rays. M. BALTRUSCHAT AND H. STARKE. *Physik. Z.* **23**, 403-16(1922).—An influence-machine gives the same secondary ray emission as high tension storage cells with a hot cathode in an extreme vacuum. The emission from Pt, Al and C (lamp black) was detd. under different conditions. The reflecting material must be charged negatively; otherwise the very slow moving secondary rays are held back. Up at 6000 primary v. only very few quite slow secondary rays are produced. As the voltage is increased the velocity of the secondary rays increases to a max., beyond which the apparent velocity falls again because an ever increasing fraction escapes measurement. F. O. ANDEREGG

Characteristics of electron tubes. H. GREENACHER. *Z. Physik* **11**, 239-52 (1922).—The validity of the $3/2$ power law of Langmuir and Barhaussen has been established for cylindrical tubes if in place of the actual voltage the algebraic sum of applied voltage, the heating voltage, the energy emission of the electrons and the contact potential is substituted. The proportion of the electrons penetrating the gauze electrode may be detd. by measuring the emission current and the gauze current with an insulated anode. Some measurements were made of the potential of the charged anode. Detn. of the consts. for the Langmuir-Barhaussen formula leads to the conclusion that a correction factor must be applied for non-cylindrical tubes. Expts. are given as to the magnetic effects of the electron current with reference to the method of e/m detn. F. O. ANDEREGG

Quantum applications not limited to periodic systems. ADOLF SMEKAL. *Z. Physik* **11**, 294-303(1922).—The soln. of the equations of motion according to the quantum theory cannot be carried out without limiting them to a periodic mech. system of f degrees of freedom. By making such limitations sharp quantization may be obtained for pure at. problems. In this way a successful treatment of intermol. reactions, such as translation of the mols. and their collisions, may be made. F. O. ANDEREGG

Electron discharge with small electrode intervals. FRANZ ROTHER. *Physik. Z.* **23**, 423-7(1922); cf. *C. A.* **9**, 15 and Hoffmann, *C. A.* **15**, 2384.—A method has been worked out for the accurate measurement of the infinitesimal currents when small voltages are applied in a high vacuum between highly polished spherical electrodes spaced at very short intervals. Results are promised. It is pointed out that polishing will orient the atoms in the surface in different directions so as to produce more or less of a point effect. F. O. ANDEREGG

The ionization of mercury vapor in the presence of argon. GEORGES DÉJARDIN. *Compt. rend.* **175**, 1203-6(1922).—The effect of A on the ionization of the vapor of Hg ionized by electrons of varying speeds is similar to that for He. Its effects are chiefly three: (1) The curve representing the variation of the electronic current as a function of the accelerating potential gives 2 distinct breaks. The first indicates the beginning of the ionization of Hg by direct impact; the second results from an increase of ionization, which depends on the pressure of A. (2) When A is present the luminosity at the electrodes begins at a much lower voltage. (3) The spectrum is also changed. There is first only the strong line of Hg but when the potential of illumination is passed the arc spectrum of Hg and the red spectrum of A appear. At 20 v. line 3984 of Hg appears and at 35 v. the blue spectrum of A. These effects are explained by assuming that the gas emits a resonance radiation which ionizes the Hg. MARIE FARNSWORTH

Thermionic effects caused by alkali vapors in vacuum tubes. IRVING LANGMUIR AND K. H. KINGDON. *Science* **57**, 58-60(1923); cf. *C. A.* **17**, 27.—Cs forms an adsorbed layer on a W filament owing to the fact that the electron affinity of a W surface is greater than that of Cs ions. On heating, the Cs evaps. off as neutral atoms as it has a greater

electron affinity than that of a W surface covered with Cs. When 20% of the W surface is covered with Cs atoms, the electron affinity of the surface is the same as that of the Cs ions. With less Cs present it leaves as positive ions. An equation is developed from the kinetic theory which affords an accurate method of detg. the vapor pressure of the alkali metals from the positive ion generation. Cs will not form a layer on a filament with an adsorbed film of Th which has a smaller electron affinity and a more stable film is formed in the presence of traces of electronegative gases. M. FARNSWORTH

The process of light radiation from an atom of a gas leading to a possible interpretation of Planck's quantum by means of electrodynamics. IV. A. C. CREHORE, *Phil. Mag.* **45**, 34-64(1923).—Using the model for the H atom developed in part I (*C. A.* **16**, 377) the effect is examd. electrodynamically of the passage of a stream of electrons near but not colliding with the H atom. Saha's formula for pondermotive force is applied. The principal underlying the treatment is that the high-frequency vibrations of the elementary charges and the radiation of energy in quanta are caused by the temporary ejection of an electron from the atom which in most cases returns to it again. On the assumption a formula is deduced which takes the general form of the quantum expression $E = h\nu$, and reduces to it. For the details of the elegant method of treatment one must be referred to the original. One of the most important conclusions is that the total energy content of the elementary positive and negative charges is of the utmost import as being the key to most at. actions, because it is drawn upon temporarily in radiation, and in the dissociation of mols. in all chem. reactions and probably in all at. phenomena. S. C. LIND

Cathode disintegration. RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO., LONDON. *Phil. Mag.* **45**, 98-112(1923).—A triode arrangement is used consisting of a spiral W cathode heated by a 6-v. battery, and a plate anode of Ni. Between the two, extending entirely across the discharge chamber and terminating in 2 in-sealed terminals, is a grid in the form of a close spiral of fine W wire such as is used for gas-filled lamps. The grid is made negative toward the hot cathode and hence receives positive gas ions, which arrive with sufficient energy to produce disintegration of the W spiral. The disintegration is measured by the change in elec. cond. One would not expect decrease in cond. to be a reliable measure of loss of wt. by the spiral, but an analysis of its behavior shows it to be well suited to the purpose. The preliminary results show that disintegration is independent of the temp. up to 1200°, that it increases regularly with the energy of the positive ions and becomes appreciable when the energy is not greatly above that required to ionize the gas. There is no irregularity in the neighborhood of the normal cathode fall. The disintegration in different gases increases in the order H, He, N, Ne, Hg, A, indicating increase with at. mass, but showing a reversal in the case of Hg and also of Na (preliminary only). For a given gas the disintegration S has the form: $S = a(V - V_0)$, where V_0 , the threshold voltage, is about 100 v. and a is a const. characteristic of each gas. Incidentally some results on the disappearance of the gases were also recorded which show that the quantity is primarily dependent on the positive ionization or satn. current rather than on the quantity of splashed metal. The latter cannot be regarded as trapping the gas but probably does furnish fresh surface for its deposition and retention. In the cases of Ne, He, and N the gas occluded is proportional to the current within a factor of 4. No calcn. appears to have been made of the Faraday equiv. Of the 3 gases N is the most and He the least occluded. S. C. LIND

The molecular scattering of light in dense vapors and gases. C. V. RAMAN AND K. R. RAMANATHAN. *Phil. Mag.* **45**, 113-28(1923); cf. *C. A.* **17**, 677.—It is shown that the scattering from unit vol. of a gas is proportional to the abs. temp., to the square of the d , and to its compressibility. Therefore if the gas obeys Boyle's law, the law

for the scattering reduces to Rayleigh's, but for gases or vapors not obeying it the Einstein-Smoluchowski formula is followed, as has been confirmed by expts. with Et_2O vapor and liquid over a range of temp. below and above the crit. point. An appended note states that in still more recent expts. on the scattering of light in the vapors of benzene and pentane at different temps. and also in CO_2 at high pressure the applicability of the Einstein-Smoluchowski formula is confirmed and it is shown definitely that Rayleigh's law is valid only in gases obeying Boyle's law. S. C. LIND

The motion of electrons in carbon dioxide. M. F. SKINNER. *Phil. Mag.* **44**, 994-9(1922).—Using an app. similar to that of Townsend and Bailey (*C. A.* **16**, 681, 2070) for H, N, O and A, S. has reported the following results for CO_2 , where p is pressure in mm. Hg, k the factor by which the kinetic energy of the electron exceeds that of a mol. of gas at 15° , W is the velocity in cm./sec. of electrons in the direction of the elec. force, Z is the voltage drop per cm., l is the mean free path of electrons in cm., u is the velocity of agitation of electrons in cm./sec. where $u = 1.15 \times 10^7 \sqrt{k}$, and λ is the proportion of energy of an electron lost in collision with a mol. $W = (Z/p)(e/m)(lp/u)$ 0.815 and $\lambda = 2.46 W/u^2$.

Z/p .	k .	$W \times 10^{-4}$.	$u \times 10^{-4}$.	$lp \times 100$.	$\lambda \times 10^4$.
50	139	19.5	135.7	3.67	506
40	117.5	17.75	124.8	3.84	497
30	96	15.9	112.8	4.15	487
20	75	13.8	99.5	4.76	472
10	47	10.8	78.9	5.91	460
6.5	20.7	7.8	52.4	4.36	543
5.0	9	5.0	34.5	2.39	516
4	4.8	3.2	25.2	1.40	397
3	2.3	2.0	17.5	.809	321
2	1.8	1.18	15.4	.630	144
1	1.5	.55	14.1	.538	37.4
0.5	1.3	.25	13.1	.454	8.95
0.25	1.2	.12	12.6	.419	2.34

S. C. LIND

The ultimate radiations of elements in spectral series and their relation to resonance radiations. F. CROZK. *Compt. rend.* **175**, 1143-6(1922).—A discussion of the radiations which persist longest when the concn. of an element in spectrum analysis is indefinitely decreased and the relation of these radiations to resonance radiations which first appear when elements are bombarded by means of electrons whose kinetic energy is progressively increased. The heads of certain spectral series disappear last in spectrum analysis. According to Bohr's theory the resonance radiations are those lines for which the least expenditure of energy is necessary. They are consequently those lines which would have the greatest chance of persisting when the concn. of the element is diminished. Hence, a correspondence between these resonance radiations and those lines in the spectrum which disappear last, might be expected. A comparison of the observations shows that in many cases this relation exists. A. W. SMITH

Corpuscular spectra and the photoelectric effect. MAURICE DE BROGLIE AND LOUIS DE BROGLIE. *Compt. rend.* **175**, 1139-41(1922).—A discussion of the conclusion of Whiddington concerning the conditions under which corpuscular spectra are emitted. Some supplementary observations (*C. A.* **16**, 381, 2264) are made on I, Ba and Sa. These results show that corpuscular spectra emitted from a certain level are diminished but do not disappear when their energy becomes less than the energy characteristic of that level. An expression is given for the intensity of the corpuscular spectra excited by radiations of frequency ν for the same level of different elements. This ex-

pression which is a function of the at. no. passes through a max. and then decreases rapidly when the at. no. is increased. In the study of the photoelec. effect in the visible and near ultra-violet region of the spectrum, Millikan found that the energy of the photoelectrons is given by $h\nu$, where ν is the frequency of the incident light. If the electrons in the photoelectric effect are more or less free electrons and if the quantum of light $h\nu$ in these expts. does not exceed the first ionization potential for the metal, there is nothing contradictory in these results on the photoelectric effect in the visible and the authors' view concerning the photoelec. effect for X-rays. A. W. SMITH

The ultra-violet absorption spectra of alkaloids of the group of isoquinoline. Papaverine and its hydrochloride. PIERRE STEINER. *Compt. rend.* 175, 1146-9(1922).—The absorption spectra of papaverine dissolved in ether and in alc. and its hydrochloride dissolved in water and in alc.-ether have been studied in the ultra-violet region of the spectrum. These absorption spectra are compared with the absorption spectra of isoquinoline and veratrole. Papaverine in ether soln. shows 4 absorption bands. Two of these are narrow and two are wide. For the aq. soln. of the hydrochloride there is one broad band without a well defined max., followed by a second more intense and well defined band. The absorption of papaverine is not represented by the curve obtained by adding the curves for its constituents, isoquinoline and veratrole, but it is a fairly accurate image of the absorption curve of isoquinoline, simplified and displaced toward the red end of the spectrum. The absorption is somewhat greater in papaverine than in isoquinoline. The absorption of this alkaloid is detd. by the isoquinoline group. The veratrole group plays only a secondary part. Its introduction into the mol. causes only a simplification, a displacement and an increase of the absorption. The absorption spectrum of papaverine is the same in ether and in alc. In the hydrochloride there is a complete fusion of the 4 bands of papaverine. The curve is displaced toward the red and the absorption is augmented a little. The absorption between $\lambda = 3216$ and $\lambda = 3117$ Å. is characteristic of papaverine. A. W. SMITH

Absorption of light by chlorine. H. V. HALBAN AND K. SIEDENTOPF. *Z. physik. Chem.* 103, 71-90(1922).—The absorption by Cl of light between 254 and 643μ (Hg, Zn, and Cd lines) and between 383 and 451μ (nitra lamp) has been measured quant. with the photoelec. two-cell arrangement previously described (cf. C. A. 16, 2078). Within the pressure range studied (0.1 to 1.0 atm.) Beer's law holds. The absorption curve shows a max. in the ultra-violet at about 334μ and a min. in the yellow. From the yellow to the red the absorption increases and reaches a second max. probably between 614 and 643μ . Apparently there is no difference between the absorption of light by moist and dry Cl. H. JERMAIN CREIGHTON

Action of light on arsenic trisulfide hydrosol. RAY V. MURPHY AND J. H. MATHEWS. *J. Am. Chem. Soc.* 45, 16-22(1923).—The elec. cond. of As_2S_3 hydrosol increases upon exposure to light, the rate of change increasing somewhat with decreasing concn. of the colloid, owing to the increased photochem. activity of the colloid per unit mass of As_2S_3 , brought about by the greater dispersity of the more dil. sol. The reaction is explained, following Freundlich and Nathanson, as one of a 2-stage photochem. oxidation of H_2S to colloidal S and a thionic acid, accompanied by reaction between H_2S and the thionic acid which serve as stabilizing electrolytes for micelles of As_2S_3 and S, resp. Removal of the stabilizing electrolytes produces destabilization of the 2 colloids which are pptd. The increase in cond. is due to the building up of a concn. of the thionic acid sufficient to serve as the stabilizing electrolyte for the colloidal S, the reaction between H_2S and the thionic acid then proceeding at such a rate that equil. is maintained. Further change in cond. is thus prevented. E. P. WIGHTMAN

Spatial progress of photochemical reactions in jellies. A. BENRATH AND K. SCHAFF. GANZ. *Z. physik. Chem.* 103, 139-54(1922).—The spatial progress of photochem. re-

actions has been investigated. If jellies absorb effective radiations, the reaction proceeds in accordance with Lambert's law. If the absorption of effective radiation is not appreciable, then the progress of the reaction is proportional to the time. Expts. on the decompn. of Cl water contained in jelly show that the ClO-ion is the light-sensitive component. The permeability of org. jellies for ultra-violet radiation is very marked, while that of animal skins is extremely small. H. JERMAIN CREIGHTON

Photochemical catalysis. E. C. C. BALY. *Rec. trav. chim.* 41, 516-29(1922).—An address in which B. describes his quantum theory based on new assumptions. In the latter part he reviews his recent expts. on the synthesis of hexoses and amino acids from CO₂ in the presence of sunlight and aq. solns. of malachite green. Cf. C. A. 15, 3072; 16, 3463. E. J. WITZEMANN

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4—ELECTROCHEMISTRY.

COLIN G. FINK

Commercial electro-thermic processes. II. BRUNO WÄRSER. *Chem.-Ztg.* 46, 928-30(1922); cf. C. A. 16, 4142.—The methods of fusing silica and the use of elec. furnaces in melting and mfg. Fe and Fe alloys are briefly surveyed. Among the alloys of Fe are included those with Si, Mn, Al and Ti. III. *Ibid* 947-8.—The manuf. of ferro-Cr, ferro-Ni, and ferro-Mo, CaC₂, Al, P and CS₂ are briefly reviewed. Numerous places are mentioned at which the processes are being carried out. IV. *Ibid* 970-2.—Brief review of Zn melting and refining, manuf. of cement and steel; use of elec. heating in coal distn., fixation of N₂ in the arc; and elec. steam generation. M. K.

The manufacture of fine forging steels. L. J. BARTON. *Blast Furnace and Steel Plant* 10, 612-8(1922).—Basic elec. furnaces are considered. Hearth and bottom should be made by burning in the refractory bit by bit and not by ramming and then burning. Short electrodes are placed on the brick bottom, basic open hearth, or blast furnace, slag is then dusted over the bottom and melted down, then addns. of dead-burned magnesite are dusted from time to time as temp. for setting the bottom rises. The drying-out period should take from 12 to 24 hrs. depending on the moisture content

of the refractories. When the furnace is at about 600° the electrodes are lowered and the bottom is gradually sintered in. Good scrap should be used, lime should be thoroughly burned and crushed to 1/2 in. or smaller; fluorspar should contain over 85% CaF_2 ; the recarbonizing materials should be low in ash and S. The working of C-, Cr-, and Ni-steels is discussed with a typical heat for each type given in detail. The Cr addn. for Cr-steel should be made 20-30 min. before tapping. Trouble is encountered in wildness with Ni-steel heats. Ca silicide is recommended to eliminate over oxidation. For V steels the V addns. should be added not over 10-12 min. before pouring. Slag inclusions are prevented by: (1) pouring superheated metal and holding in the ladle; (2) adding a small amount of CaF_2 to the ladle, (3) using ferro-Ti in the ladle. Ingots should be cast large end up and a "hot top" used.

C. H. HERTY, JR.

Manufacture of phosphoric acid in the electric furnace by the condensation and electric precipitation method. THEODORE SWANN. *J. Ind. Eng. Chem.* **14**, 630-1 (1922).—A mixt. of phosphate rock, coke, sand, and Fe borings is smelted in an elec. furnace producing ferro-P contg. 24-25% P and liberating P with other furnace gases which are oxidized by air and drawn out of the furnace into the condensing and elec. pptg. app. The acid obtained contains 90-95% H_3PO_4 with little impurity.

W. H. BOYNTON

Notes on the electrodeposition of iron. H. D. HINELINE. *Trans. Am. Electrochem. Soc.* **43**, preprint(1923).—Careful study was made of the problem of depositing Fe on rubber and on Fe. Surfacing with graphite after varnishing rendered the rubber conducting. Best bath found contained equal parts of FeCl_3 and CaCl_2 in such quantity as to sat. the bath at 30° to which was added per l., 20 g. CrCl_3 , and 5 g. hydroquinone. Temp. = 60-70°, density = 8 amp. per sq. dm. A good deposit, 1 cm. thick, free from pitting and excessive treeing, was obtained. The deposit had the strength of mediocre cast Fe. It is absolutely necessary to keep the bath reduced; this was done best with the hydroquinone. This was oxidized at the anode to quinone and in turn reduced by H_2 at the cathode, again forming hydroquinone. This removal of H_2 at the cathode helps to avoid pitting. Earlier baths, such as those of Fisher-Langbein, and Hughes were tried out. The action of the CrCl_3 is not well understood nor is its effect marked. Analysis of cathode shows 0.3% Cr, which seems to promote a finer deposit. Acidity may range from 0.01 to 0.5% HCl without causing excessive brittleness. The bath lacks "throwing" power, and will plate over depressions in the rubber without filling them, unless special steps are taken.

CHAS. H. ELDRIDGE

Electrodeposition of copper. I. W. E. HUGHES. *Beama* **12**, 19-26(1923).—In detail is described the practical operation of the alk. cyanide, and of the acid plating baths. Alk. cyanide bath is recommended for thin platings and must be used for plating on Fe, as follows: *Compn. and working conditions.*—To 1 l. of H_2O add 52.5 g. KCN and 33 3/4 g. Chevreul's salt. Dissolve KCN in hot H_2O , add Cu soln., and then dil. Filter off any brown solid ("paracyanogen"). To make Chevreul's salt dissolve 480 g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 2 l. H_2O at 60-70°, and add while hot 840 g. Na_2SO_3 dissolved in hot H_2O . Wash the resulting red cryst. ppt. which should have a yield of 53 per 100 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Chevreul's salt has the compn. $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_4 \cdot 2\text{H}_2\text{O}$, if made as above. The sulfite acts to keep anodes clean. For working conditions use 3-4 amp. per sq. ft., 9-11° Bé., temp. 18-49°, preferably the latter. *Electrode reactions* are still a matter of theory. The author prefers the secondary metal theory of Classen. *Operation.*—Under this heading are discussed care of anodes, regeneration of solns., and a table is given detailing defects, their causes and remedies. The acid sulfate bath should be used for all thick deposits, and is by far the most important one. *Compn.*— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (240 g. per l.) 5 to 10% of H_2SO_4 . *Working conditions.*—Sp. gr. = 14-16° Bé., c. d. = 10-15 amp. per sq. ft., without agitation or 15-20 amp. with agitation. E. m. f. = 2-3 v. Use

good grade com. metal. *Operation*.—Although seeming simple this bath requires care of many details to obtain desired deposit. Especially for thick deposits the soln. must be kept clean. A simple filter is recommended. A detailed table is given of defects, their causes and remedies.

CHAS. H. ELDRIDGE

The role of colloids in electrolytic metal depositions (addition agents). H. J. SAND. *Brit. Assoc. Advancement of Sci., 4th Rept. 1921*, 346–56.—Following a brief historical review, S. considers the phenomena produced by addn. agents; their colloidal nature and inclusion in the deposited metal; their gold-number and adsorption relative to their effectiveness; their action after adsorption; microstructure of deposits; equil. potential, transfer-resistance and polarization; over-voltage effects; mechanism producing the final structure of electrolytic metal deposits; importance of colloidal substances accidentally present or incidentally produced; colloids at the anode; colloids in applied metal deposition. An extensive bibliography is appended.

J. A.

The electrolytic production of lead arsenate. J. F. CULLEN AND T. E. HARPER. *J. Ind. Eng. Chem.* **14**, 651(1922).—A graph is shown to supplement data (cf. *C. A.* **16**, 1708) on, and to summarize the best conditions for, the electrolytic production of Pb arsenate. The arsenate of acid type is cryst. and of large dry bulk while that of the basic type is amorphous and of small dry bulk. Both have good suspension quality.

W. H. BOYNTON

Crystalline deposition of metals by electrolysis with high current densities. I. LEAD. A. GÜNTHER-SCHULZE. *Z. Elektrochem.* **28**, 119–22(1922).—It is shown how the form of the deposit is influenced by the geometrical arrangement of the electrodes on the one hand, and the dependence of the rate of deposition on the “crystal-direction” on the other. The dependence of the rate of crystal growth on the current strength has been studied in the case of the deposition of Pb from satd. $\text{Pb}(\text{NO}_3)_2$ solns. Between 100 and 140 milliamp. the rate of growth increases rapidly with the current strength, above and below these limits much less rapidly. The rate of growth of the Pb crystals from $\text{Pb}(\text{OAc})_2$ decreases rapidly if the dissociation of $\text{Pb}(\text{OAc})_2$ is depressed by the addition of NaOAc . From a soln. contg. Pb and Cu ions, practically only the former ion is deposited with a current d. of about 60 amp./cm².

H. JERMAIN CREIGHTON

Relation between the maximum velocity of electrolytic deposition and the hydration of the metal ions. (Lead.) A. GÜNTHER-SCHULZE. *Z. Elektrochem.* **28**, 122–6(1922); cf. preceding abstract.—The investigation of the cryst. deposition of Pb from satd. solns. of $\text{Pb}(\text{NO}_3)_2$ shows that the satn. current is attained in 3 different directions with 3 essentially different current strengths. In the most favorable direction the max. possible velocity of deposition is 0.206 cm./sec. of Pb. From this it is calculated that the av. time required for the deposition of one Pb ion is $1.5 \cdot 10^{-7}$ sec., and the current d. at the axis of the growing crystal filament is 220,000 amp./dm². The dependence of the satn. current on direction may be linked up with the mode of hydration of the Pb ions.

H. JERMAIN CREIGHTON

Electrode for the evolution of oxy-hydrogen gas. (Aluminium.) A. GÜNTHER-SCHULZE. *Z. Elektrochem.* **28**, 126–9(1922).—With 2 Al electrodes of the same size, O and H are evolved in NaPO_3 soln. by an a. c. of 50 cycles as though each phase were present alone. No appreciable depolarization of the products of one phase is brought about by those of the next phase.

H. JERMAIN CREIGHTON

The throwing power of plating baths. KURT ARNDT AND OSKAR CLEMENS. *Chem.-Ztg.* **46**, 925–6(1922).—There are 2 resistances opposing the flow of current, one, the ohmic of the bath and the other, an electrode surface resistance. When the plating begins the tendency is toward more deposition on the parts of the article nearest the anode, but this decreases the ion concn. near those parts and gives rise to a concn. polarization that diminishes the current there. Relatively more current can then flow

to the parts farther away from the anode. This viewpoint leads to the conclusion that the throwing power will increase the fewer metal ions there are in soln. to begin with and the better the bath conducts; for with increasing cond., the differences in the resistance of the various paths become less. Expts. were made with two 7×7 cm. cathode plates, one plate being between the anode and the other plate and having a hole 2 cm. diam. through which the current must pass. Maintaining the cond. of a NiSO_4 plus NH_4Cl bath const. but decreasing the Ni concn. increased the relative amt. of Ni deposited on the 2nd cathode as predicted. Also maintaining the Ni concn. const. but increasing the cond. of the soln. favored deposition on the second cathode. A comparison between a sulfate and cyanide bath of Cu gave 38% deposition on the second cathode for the cyanide against 7% for the sulfate bath which was expected on account of the small Cu^{++} concn. in the cyanide bath. Increase of temp. and stirring decrease the throwing power of a soln. by lessening the concn. polarization. M. KNOBEL.

Notes on galvanic cells and dry batteries. FRIEDRICH LEHNER. *Chem.-Ztg.* **46**, 37-8(1922).—Dry cell reactions consist of ionization of Zn at the cathode and either discharge of NH_4^+ or reduction of Mn^{+++} at the C anode. The soln. in the cell is NH_4Cl and ZnCl_2 which must be free from Fe, Pb, Cu, As, Ni, Co, and Sb to avoid local action and from SO_4 to avoid formation of insol. (?) sulfates. The MnO_2 depolarizer must be porous and finely divided to aid absorption of H_2 ; graphite is mixed with it to increase its elec. cond. The short circuit current from the battery is a measure of its internal resistance. The resistance increases with age, owing mainly to formation of basic zinc chlorides on the Zn and partly to drying out. A discharge curve for a battery through 15 ohms shows an approx. uniform drop in voltage from 4.65 to 1.85 in 4 hrs. The voltage of another cell not delivering current dropped from 5.00 to 4.50 in 3 months and to 4.16 in 6 months. M. KNOBEL.

Theoretical studies on the change of density of the electrolyte within the pores of the storage battery plates during discharge. HIROMU TANAKA. *J. Chem. Ind. (Japan)* **24**, 1268-72(1921).—With the following assumptions, the change of d. of the electrolyte within the pores of the plate during discharge is calcd.: The pores are considered to be small tubes, having the same length; lines of elec. current are equally distributed within the plate during the discharge, and same throughout the discharge. During the discharge, the amt. of H_2SO_4 is used up within the pores, thus lowering the d. of H_2SO_4 in the pores. The H_2SO_4 outside of the pores then diffuses into the pores. When the density of the electrolytes in the pores becomes equal to that of the outside of the plate, then there will be equil. If Q_m is designated as the concn. of the electrolytes within the pore at this point of equil., and Q_o , concn. of the electrolytes outside of the plate and Q_i that of within the pore, the following relationship will hold. $Q_m = (Q_o/3) + (2Q_i/3)$. S. T.

The corrosion of lead-covered cables by electrolytic action. S. C. BARTHOLOMEW. *Electrician* **90**, 69(1923).—The chief systems of protection against electrochem. corrosion are based on the limitation of stray currents. The divergence between Brit. and Am. methods of protection is pointed out. Cables should be kept away from elec. railway lines. Direct or indirect contact with rails should be avoided in a "negative" area and drainage connections in a "positive" area require careful study. Earth plates should be sunk, to which cables and pipes are connected at boxes near the points where the current leaves the cables. Cables should be kept clear of the water in boxes and man-holes and should not be connected to earth plates positive to them. W. H. BOYNTON.

New equation for the static characteristic of the normal electric arc. W. B. NORTINGHAM. *J. Am. Inst. Elec. Eng.* **42**, 12-9(1923).—The normal arc is defined as one in which the current intensity is greater than the max. for the glow arc and less than the min. for the hissing arc, and which is free from external elec., magnetic, atm. and phys.

disturbances. If the arc length is assumed to be const. the Ayrton and the Steinmetz equations can be written $E = A + (B/i^n)$, in which E is the p. d. across the arc, i the current flowing in the arc, A and B are consts. depending on the arc length and n is a const. dependent only on the electrode material. n is detd. for arcs in air between cathodes of C and anodes of C, Cd, Cu, Al, Ni, Ag, Zn, Pb, Sb, and Bi and found to be proportional to the abs. temp. of the b. p. of the anode material. The anode material is taken to be the oxide in the case of Cd, Cu, Al, Ni, and Zn anodes. The static characteristics of the normal arc can be represented without apparent systematic error by an equation (see original) involving arc length, arc current and n . D. MACRAE

Neon glow lamp. ARTHUR PALME. *Elec. World* 81, 216(1923); 3 illus.—A new signal and decorative lamp for use on 220 v. It consists of 2 electrodes placed together and enclosed in a rarefied atm. of Ne gas. Min. voltage of 130 a. c. or 180 d. c. is required to operate lamps. On a. c. both electrodes glow with a pleasing pinkish orange light with a violet fringe. At 220 v. the wattage is about 2, and intensity is about 1 c. p. With d. c. only one electrode glows; with a. c., both appear to be simultaneously luminous at 60 cycles. Electrodes may be shaped like numbers or letters and are very conspicuous even in daylight. CHAS. H. ELDRIDGE

Heat insulating materials for electrically heated apparatus. J. C. WOODSON. *Trans. Am. Electrochem. Soc.* 43, preprint(1923).—While there are numerous grades of heat insulators, none can compare with elec. insulators. Of all the various grades there are only a few basic materials used. True insulation value lies almost entirely in the entrapped dead air spaces of the structure, and this goes back to the phys. structure of the cell or crystal. Working temp. ranges may be grouped under 5 divisions: below 93°, 93–177°, 177–315°, 315–538°, 538–1093°. To cover these temp. ranges, practically all com. grades of insulators can be grouped into 3 classes as follows.—Class A, —18° to 93°, hair, wool, felt, wood pulp, animal and vegetable fiber, asbestos paper and cork; Class B (most important), 93–538°, magnesite, sponge, earths, mineral wool and asbestos; Class C, 315–1093°, diatomaceous earth, mineral wool, earths and silicates. Since the law of heat flow is analogous to Ohm's law 2 formulas are given. For flat surfaces with the customary units the formula is: $Q = KA [(T_1 - T_2)/d]$, where Q = B. t. u. transmitted, A = sq. ft., t = time in hrs., d = thickness in inches, $T_1 - T_2$ = °F., and K = coeff. of thermal cond. = B. t. u. per sq. ft., per inch of thickness, per hr., per Fahrenheit degree. For cylindrical surfaces $Q = \frac{K(T_1 - T_2)}{R \log_e (R_2/R_1)}$, where R_1 = inside radius of covering in inches and R_2 = outside radius. The numerous attributes desired in insulators are outlined. Complete tables are given showing attributes of many com. grades. Curves are given which show that the const. K does not increase directly with thickness, and that its value is not const. for all temp. differences. CHAS. H. ELDRIDGE

Transformer oils—German specifications. G. STERN. *Elektrotechn. Z.* 43, 140–3 (1922). C. G. F.

BANGERT, KARL: *Masse und Masssysteme mit besonderer Berücksichtigung der Elektrotechnik.* Frankfurt a. M.: Kesselringsche Hofbuchh. 110 pp. M 22.50.

GRUBE, GEORG: *Grundzüge der angewandten Elektrochemie.* Bd. I. Dresden & Leipzig: Th. Steinkopff. 268 pp. M 70. Bound M 86.

HUGHES, W. E.: *Electro-Deposition of Iron.* With an Appendix containing a bibliography. London: H. M. Stationery Office. 50 pp. 6s. 6d. Reviewed in *Nature* 110, 445(1922).

MEYER, OSWALD: *Elektrische Öfen.* Berlin and Leipzig: Vereinigung Wissenschaftlicher Verleger. 133 pp. 30 cents. Reviewed in *Proc. Am. Soc. Civil Eng.* 49, 33(1923).

Storage battery. S. M. MEYER and W. JAMES. U. S. 1,440,023-4, Dec. 26. Structural features.

Storage battery plate. J. N. HANNA. U. S. 1,440,354, Dec. 26. Structural features.

Storage battery electrode. C. GROSS. Brit. 187,583, Sept. 19, 1922. A positive electrode for an accumulator consists of an oxide of a metal capable of forming a no. of oxides such as Mn, together with an O-transmitting catalyst such as a metal of the Pt group, Pb superoxide, etc. The mixt. may be pressed into the form of a plate or it may be attached to a grid. The mass may be rendered porous by adding a Cl or Br compd. of the metal whose oxide is used, the halogen being subsequently removed by chem. or electrolytic means. *E. g.*, MnO_2 is added to a satd. soln. of MnCl_2 contg. 1% of PtCl_2 to form a dough which is pressed into the form of a plate or introduced into a metal grid. This is then dried and made the anode in an electrolytic bath of dil. H_2SO_4 until all the Cl is expelled.

Storage battery electrode. C. GROSS. Brit. 187,584, Sept. 19, 1922. A negative electrode for an accumulator consists of an oxide of a metal capable of forming a no. of oxides such as Mn together with a H-transmitting substance such as Pd or a metal of the Pt group. The mixt. may be pressed into the form of a plate or it may be attached to a grid. The mass may be rendered porous by adding a Cl or Br compd. of the metal whose oxide is used, the halogen being subsequently removed by chem. or electrolytic means. In an example Mn_2O_3 is added to a satd. soln. of MnCl_2 to form a dough which is pressed into the form of a plate or introduced into a metal grid. The plate is then dried and placed in H_2SO_4 whereby a part of the halogen is liberated, the plate being then ready for use as an accumulator electrode. During the first charge the Mn_2O_3 is reduced to MnO and during the subsequent discharge the remaining halogen is liberated.

Desulfating storage battery electrodes. W. O. GARBUTT. U. S. 1,441,792, Jan. 9. Sulfated Pb electrodes are sepd. from the H_2SO_4 electrolyte with which they have been used and are then subjected to charging by current of ordinary charging d. while immersed in a strong alk. soln., *e. g.*, NaOH. Cf. C. A. 17, 242.

Storage battery electrolyte. A. POUCHAIN. Brit. 188,027, July 21, 1921. Addn. to 170,618 (C. A. 16, 1048). The storage battery electrolyte described in the principal patent is modified by the addn. of a hydrocarbon of high b. p. such as vaseline oil. This electrolyte or the one described in the principal patent is treated by passing an elec. current through it in the presence of metallic Hg. Alternating or continuous current may be used. In the former case both electrodes are of Zn; the cathode is of any other metal when continuous current is used.

Thermoelectric batteries. DRIVER-HARRIS CO. Brit. 186,792, Aug. 29, 1921. An element for a thermocouple consists of Cu, Ni and Cr. The proportions may be Cu 50-75, Ni 25-50, and Cr 5-30 parts. The other element of the couple may consist of Fe or a Ni-Cr alloy. The latter may consist of Ni 100 and Cr 10 parts.

Electrolytic cell for oxygen and hydrogen or other gas production. A. K. SMITH. U. S. 1,442,238, Jan. 16. Electrodes for cells adapted for treating aq. alk. solns. are formed with a body of base metal coated with Ni or Co with a superficial layer of oxide or hydroxide of Ni or Co in porous, adherent, conductive condition, which reduces over-voltage.

Cathodes for accumulators with acid electrolytes. ADOLFO POUCHAIN. Holl. 7327, May 8, 1922. A conducting non-metal, such as C, preferably having been coated with a thin layer of Cu, is used as cathode in a bath contg. salts of Zn, Hg, and Mg.

Cathode for batteries. M. E. FULD. U. S. 1,439,955, Dec. 26. A cathode for batteries is formed of a conductor such as Ag around which a cylinder of AgCl or other depolarizing material is molded with a spiral groove extending the length of the cylinder,

a wrapper of fibrous material and a wire (preferably Ag) pressing the wrapper into the groove and extending beyond the end of the cylinder. U. S. 1,439,956 relates also to structural features of similar batteries, with cup-shaped anode of Zn.

Stabilizing negative electrodes of lead storage batteries. R. C. BENNER. U. S. 1,439,994, Dec. 26. The electrode is washed with hot or cold H_2O substantially free from dissolved O ; most of the H_2O is removed by alc. or other volatile liquid miscible with H_2O and the residue of the volatile liquid is evapd.

Concentric cylindrical electrodes. R. A. LONG. U. S. 1,440,091, Dec. 26. A cylindrical Pt anode is mounted concentrically between 2 cylindrical cathodes which may be formed of Fe for use in electrolytic cells.

Copper alloy electrodes. C. G. FINK. U. S. 1,441,567-8, Jan. 9. An anode composed of Cu alloyed with Si 15-25, Mn 2-15, Pb 0.5-10 and Ba or Ca 0.01-10% is used for electrodeposition of Cu from $CuSO_4$ solns. Anodes of this alloy are highly resistant to anodic disintegration. *Some Fe, Sn, W, Ni or Cr may also be present in the material.

Baking carbon electrodes. C. W. SÖDERBERG. U. S. 1,441,037, Jan. 2. A conductor which may be formed of Fe is connected in parallel with a raw electrode and the raw electrode is baked by an elec. current and rendered conductive by heat electrically generated in the conductor and then further baked by heat electrically generated in both the conductor and the electrode itself. Cf. C. A. 16, 1048.

Electrolytic oxidation and reduction. C. J. THATCHER. Brit. 188,042, July 28, 1921. See Can. 222,264 (C. A. 16, 3817).

Electrolytic production of fine metal powders and colloidal solutions. J. SLEPIAN. U. S. 1,440,502, Jan. 2. A low-frequency elec. current is passed between electrodes, e. g., Cu, immersed in NaCl soln. or other suitable electrolyte, in order to form fine metal and a colloidal metal soln.

Electrolytic production of caustic alkali. H. H. DOW, T. CRISWOLD, JR. and E. O. BARSTOW. U. S. 1,441,408, Jan. 9. An aq. soln. of NaCl or similar halide is passed successively through the cathode chambers of a series of electrolytic cells of the diaphragm type and the buoyancy of the gases liberated in each cathode chamber is utilized to elevate the catholyte for transferring it to the next cell through vertical and downwardly inclined pipes.

Electrodeposition of copper from its sulfite solution. MASAO UCHINI and THE FURUKAWA KÖGYÖ KABUSHIKI KAISHA. Japan 40,137, Sept. 30, 1921. The electrolyte is prepd. by treating carbonate or hydroxide of Cu with SO_2 . With about 0.7 v. metallic Cu is deposited on the cathode alone, or together with CuS according to conditions. A C plate may be used as the anode.

Apparatus for the electrodeposition of metals. A. CRÉMER. Brit. 187,607, Oct. 17, 1922. The electrodes are arranged parallel to the flow of electrolyte in channels, groups of electrodes being sepd. by vols. of electrolyte. Each group comprises a set of parallel electrodes, alternately positive and negative, and a similar set further down the channel. Members of the two sets which lie in the same plane are of opposite polarity.

Reducing zirconium and similar rare metals. J. W. MARDEN. U. S. 1,437,984, Dec. 5. K_2ZrF_6 is heated with Al in an elec. furnace *in vacuo* or in an inert atm., first to effect reduction of the Zr and then to distil the AlF_3 and KF formed, leaving Zr as a black or grayish spongy mass which may be still further heated to sinter it into white coherent metal. Halides or double halides of Ti, U, Th, V and W may be similarly reduced.

Electrical precipitation of suspended particles from gases. H. A. PROSSER. U. S. 1,441,713. Jan. 9. Gases contg. particles which are to be sepd. by elec. pptn. are

continuously treated with acid fumes as they move to the pptg. app. in order to increase the cond. of the suspended particles.

Electrical precipitation of suspended particles from gases. A. E. NESSIT. U. S. 1,440,886-7, Jan. 2. Mech. features.

Apparatus for electric precipitation of suspended matter from gases. W. A. SHEEK. U. S. 1,442,301, Jan. 16. The app. comprises electrodes mounted in pairs so that they may be jarred by swinging one electrode of each pair to bring it into contact with the other.

Apparatus for electrical precipitation of suspended particles from flue gases. L. DANE. U. S. 1,442,052, Jan. 16. A discharge electrode is placed in a flue having a frusto-conical passage with a flaring mouth at its upper end above the constricted portion.

Electric furnace operation. M. O. SEM and E. LUND. U. S. 1,442,033, Jan. 9. A conductive material such as graphite is introduced through an electrode being baked in an elec. furnace in which it is used and elec. current is passed through the material so that it becomes heated and a column of calcined material is formed under the electrode which is removed to permit fresh conductive material to descend and undergo calcination. Cf. C. A. 16, 4149.

Electric arc furnace. W. MEINERSMANN. U. S. 1,434,395, Nov. 7. The furnace operates on a. c. and is adapted for producing refined alloy steels from scrap metal. The scrap metal may be compressed to form electrode material in the operation of the furnace.

Production and use of carbon electrodes in electric furnaces. C. W. SÖDERBERG. U. S. 1,442,031. Jan. 9. In producing C electrodes in the furnace in which they are used, the lower part of the electrode is baked by heat from the furnace (the electrode being suspended by clamping it at its baked portion) and raw material is supplied to the top of the electrode, so that tensile strain in the electrode above its baked portion is avoided.

Electrodes for electric furnaces. C. W. SÖDERBERG. U. S. 1,440,724, Jan. 2. Raw electrode material is tamped into a mantle of sheet Fe or other metal which is to form part of the finished electrode and which has projections extending into the electrode mass. Elec. current is then passed through the mantle to bake the electrode.

Electric smelting furnace. E. H. ROTHERT. U. S. 1,440,106, Dec. 26. The furnace is connected with ore-roasting chambers heated from the elec. furnace itself and from which ore is fed to the furnace.

Cuprous iodide from spring water containing iodine. FRITS ELLINGER. Holl. 7989, Sept. 16, 1922. CuI is deposited on Cu electrodes when a current at low voltage is passed through spring water contg. I.

Electric conductors. WESTERN ELECTRIC CO., LTD. Brit. 188,287, May 11, 1922. A continuously loaded signalling-conductor is produced by plating Fe and Ni upon a conducting core and subsequently heating the deposit to obtain an alloy. The deposit preferably contains at least 20% of Ni. Cf. 188,688.

Removing scale from metals. G. A. AVERY and F. BAMBLETT. U. S. 1,442,243, Jan. 16. Hardened gears or similar metal articles from which scale is to be removed are subjected to an elec. current in a soln. of cleansing compn. to remove oil and other foreign matter from the surface of the metal and is then subjected to electrolytic action in a soln. of acid and washed with soda soln.

Galvanizing wheel rims. L. V. MATHER. U. S. 1,442,437, Jan. 16. As a preparatory treatment for electroplating, a saponifying oil is incorporated with the grease on the surface of the rims or similar articles and the latter are then treated with caustic alkali and sand-blasted to remove scale.

Electroplating apparatus. L. V. MATHER. U. S. 1,442,438, Jan. 16.

Electroplating apparatus. F. J. BELL. U. S. 1,442,514, Jan. 16.

Electric lighting system for color comparisons. N. MACBETH. U. S. 1,442,166, Jan. 16.

5—PHOTOGRAPHY

LOUIS DERR

Contribution to the theory of organic developers. B. HOMOLKA. *Phot. Korr.* 59, 29-31(1922).—Certain substances contg. the group $-\text{CO}-\text{CH}_2-$, such as indoxyl, its derivs. and other compds. named, act as developers, and give besides the Ag image a colored dye image which can be easily isolated. Hydrocoerulignone, which belongs neither to this class nor to the class of ordinary developers, is found to give a similar Ag and dye image. It is a true leucobase of coerulignone and stands in about the same relation to it as hydroquinone does to quinone.

L. DERR

Experimental verification of the theory of bleach-out dyes. R. KÖCEL. *Phot. Korr.* 59, 39-40(1922).—Flavinduline is a sensitizer, while rhoduline violet, of analogous structure, is not, and the difference is ascribed to the presence of the group $-\text{CH} =$ in the former. Flavinduline contains two such groups and thioflavine one. The condition is also fulfilled by anthocyanine and was proved to hold for dyes of the phenanthrazoxonium series.

L. DERR

Investigations on the latent image. A. STEIGMANN. *Phot. Ind.* 1922, 448-9. —The action of HgCl_2 , $\text{KBr}-\text{K}_3\text{Fe}(\text{CN})_6$ mixt., and others, is now explainable by the subhalide and Ag-germ theories. Expts. definitely show the presence of Ag or Ag subhalide in the well exposed parts of the image, and the probability of one or the other in the least exposed parts.

L. DERR

Theory of desensitizing. H. LÜPPO-CRAMER. *Phot. Ind.* 1922, 287-8. A. STEIGMANN. *Ibid.* 469. H. LÜPPO-CRAMER. *Ibid.* 774-5.—In support of the oxidation theory, it is pointed out that desensitizers decrease the sensitiveness of the plate to X-rays, while optical sensitizers do not affect X-ray action. Evidence supporting the oxidation theory is found in the development of plates treated with Hg salts. These continue to function as oxidizers and must therefore be absorbed by the AgBr. This therefore cannot be absorbing either sulfite or reducer, since in that case complex Ag salts or metallic Hg would be formed and the action neutralized. Presumably double salts of Ag and Hg are formed, and similar compds. are probable with dyes used as desensitizers. All characteristic desensitizers are reduced by 5% $\text{Na}_2\text{S}_2\text{O}_4$ and by Zn dust. The usual sensitizing dyes are not reduced by $\text{Na}_2\text{S}_2\text{O}_4$. It is suggested that the nascent Ag of the latent image may act like the Zn dust.

L. DERR

Use of substitution products of benzoquinone and its higher homologs for intensifying and toning photographic plates and papers. A. AND L. LUMIÈRE AND A. SEYEWETZ. *Bull. soc. franç. phot.* [3] 9, 331-3(1922).—Benzoquinone and its sulfonic deriv. reduce the Ag image in presence of H_2SO_4 and intensify or tone it in presence of alkali chloride or bromide. This property is shared by the halogenized substitution deriv. and its higher homolog toluquinone, but the naphthoquinones and anthroquinone do not possess it. Among the benzoquinone derivs. only toluquinone gives useful results for toning diapositives or motion-picture films. It gives violet-black tones with alkalis, sulfites, and alkali bisulfites.

L. DERR

Anomalous desensitizing. H. LÜPPO-CRAMER. *Phot. Korr.* 59, 51-3(1922).—A 1:120,000 soln. of phenosafranine has a greater desensitizing effect on AgI plates than one 10 times as strong. Tolusafranine, pinasafrol, and brilliant rhodulin red act similarly. The anomaly lies in the fact that strong solns. behave normally, and the effect is not present with AgBr.

L. DERR

The sensitizing of silver bromide. F. KROPP. *Phot. Korr.* 59, 47-8(1922).—Ripened AgBr emulsions, soaked in distd. water in which various metals had stood showed a perceptible increase in sensitiveness to the less refrangible rays when the metal was Pb, Sn, Zn, or Fe, a decrease with Hg, and no change with Ag or Cu, though for the last two development could be prolonged. No general conclusions could be drawn.

L. DERR

Behavior of aqueous solutions of certain salts and acids in light in presence of glycolic acid and glycol. E. VALENTA. *Phot. Korr.* 59, 82-6(1922).—Chlorides of Au, Pt, Pd, and Ir, in 10% soln. with 4 times their respective vols. of glycolic acid, were exposed to sunlight. The rapid decompn. of the Au and the less rapid one of the Pt soln. are true photochem. reactions, which do not take place in the dark. Other salts of Pt, Pd, Ir, Fe, Hg, V, Mo, U, Pb, and Se in general show a slow change in the dark which is accelerated by light.

L. DERR

A new eliminator of hypo. E. F. SHELBERG. *Am. Phot.* April, 1922, 267.—Chloramine T (Na *p*-toluenesulfochloramide) is a cheap, convenient, and satisfactory $\text{Na}_2\text{S}_2\text{O}_5$ eliminator.

L. DERR

POULENC, CAMILLE: Les produits chimiques purs en photographie: Leur nécessité; leur emploi; leur contrôle. Paris: Charles Mendel, 188 rue d' Assas. 160 pp. F. 2.50. Reviewed in *Pharm. J.* 109, 184(1922).

Photographic films. S. J. CARROLL. U. S. 1,441,142, Jan. 2. A nitrocellulose film is rendered antistatic and less combustible by coating both of its faces with a layer of a cellulose ether compn. (e. g., an ethyl cellulose compn.) before coating it with the sensitizing mixt.

Cellulose ether composition for film manufacture. S. J. CARROLL. U. S. 1,441,143, Jan. 2. A viscous flowable film-forming compn. is formed of cellulose ethyl ether dissolved in a mixt. of MeOH 50-25 and toluene 50-75 parts.

Antistatic photographic film. A. F. SULZER. U. S. 1,441,185, Jan. 2. Nitrocellulose films carrying a sensitive compn. on one face are provided with a coating on their other face formed of a moisture-retaining compn., e. g., a nitrocellulose compn. contg. glucose and glycerol, which serves to render the film "antistatic." Cf. *C. A.* 17, 498.

Transfer printing plate. DAYLIGHT FILM CORPORATION. Brit. 187,638; April 18, 1921. Portions of exposed emulsion adjacent the light-affected part of a photographic emulsion are hardened with an agent which reacts with the light-affected part of the emulsion. Also a controlling agent is used for the hardening agent. The hardening under control may be effected during or after development. In the first type of process a developer may be used contg. pyrogalllic acid as the hardening agent and Na_2SO_4 as the controlling agent in approx. the proportions 1:2. In the second type of process the hardening is effected by the action of $\text{K}_4\text{Cr}_2\text{O}_7$ in the presence of the Ag image, the controlling agent being H_2SO_4 or HCl . The printing surface formed comprises a great no. of photographically formed, extremely minute, individual protuberances, which are distributed and grouped irregularly so as to represent photographic lights and shades. The process is used for producing copies of cinematographic films in monochrome or colors. Various alternative methods are described for carrying out the process, and formulas for these alternative methods are given. Cf. 1836, 1881, 17,773, 1889, 27,957, 1908, 18,965, 1911 (*C. A.* 7, 456), 20,555, 1912 (*C. A.* 8, 875), 5100, 1915, 127,953, 135,477 (*C. A.* 14, 1268) and 172,342. Reference is also made to the use of KI in the developing compn. described in 187,932 (following pat.), and to the method of printing an unperforated film from a perforated film described in 187,933.

Transfer printing plate. DAYLIGHT FILM CORPORATION. Brit. 187,932, April 18, 1921. In the process described in 187,638 (above), KI is used in the developer to control the degree of contrast in the image. A developer is also described contg. both K, I and Na sulfite. The process is used for producing copies of cinematograph films, and in the case of a series of exposures taken under different light conditions different amts. of the iodide are used in the developer for the different sections to produce uniform gradations.

Multicolor screen for use in color photography. J. CAMILLER and A. HAY. U. S. 1,440,373, Jan. 2. A support such as glass or other transparent material is coated with a mixt. of a dyed warm gelatin mixt. or a similar tacky material with solid colored grains such as glass or "gum sandrac," the coloring material of which will not be taken up by the tacky binder used.

6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

Residual affinity and coordination. X. Salicylatotetramminocobaltic salts and the constitution of oxonium compounds. G. T. MORGAN and J. D. M. SMITH. *J. Chem. Soc.* 121, 1956-71(1922); cf. *C. A.* 16, 2479.—The salts of the salicylatotetramminocobaltic series are well defined, sol. compds. resembling the salts of the alkali

metals, so that the new salicylatocobaltamine radical $(\text{NH}_2)_4\text{Co} \begin{array}{c} \diagup \text{O}-\text{C}_6\text{H}_4 \\ \diagdown \text{O}-\text{C}=\text{O} \end{array}$ may be regarded as a compd. univalent alkali radical. It is accompanied by 1 mol. of firmly held H_2O in all its normal salts but it becomes anhyd. in its acid or H salts with the exception of the bisulfite which is hydrated like the normal salts. The singular hydration of this radical is attributed to the presence in the complex of a subsidiary coordinating center due to the O of the unsatd. $=\text{CO}$ group. This electronegative O atom coordinates either with H_2O in the hydrated normal salts or with a hydron in the acid or H salts and in the latter case giving rise to oxonium salts. The bisulfite is exceptional in contg. the hydrated form of the salicylatocobaltamine radical, probably because the H of the bisulfite group is tied up in an electronegative complex. Nineteen compds. contg. the new radical have been prepd. Designating the radical as written above as R their formulas may be written as follows: $(\text{R} \cdot \text{H}_2\text{O})\text{Cl}$, $(\text{R} \cdot \text{H}_2\text{O})\text{Br}$, $(\text{R} \cdot \text{H}_2\text{O})\text{I}$, $(\text{R} \cdot \text{H}_2\text{O})_2\text{Hg}_2\text{Cl}_2$, $(\text{R} \cdot \text{H}_2\text{O})_2\text{Hg}_2\text{Br}_2$, $(\text{R} \cdot \text{H}_2\text{O})_2\text{Hg}_2\text{I}_2$, $(\text{R} \cdot \text{H}_2\text{O})\text{IO}_3(\text{H}_2\text{O})_2$, $(\text{R} \cdot \text{H}_2\text{O})\text{NO}_2(\text{H}_2\text{O})_2$, $(\text{R} \cdot \text{H}_2\text{O})_2\text{SO}_4(\text{H}_2\text{O})_2$, $(\text{R} \cdot \text{H}_2\text{O})_2(\text{SiF}_6 \cdot 2\text{H}_2\text{O})$, $(\text{R} \cdot \text{H}_2\text{O})_2\text{C}_2\text{O}_4$, $(\text{R} \cdot \text{H}_2\text{O})\text{SO}_3\text{C}_6\text{H}_5$, $\text{NH}_3(1,8)$, $(\text{R} \cdot \text{H}_2\text{O})\text{OC}_6\text{H}_4(\text{NO}_2)_3(2,4,6)$, $(\text{R} \cdot \text{H}_2\text{O})_2\text{CO}_3 \cdot \text{H}_2\text{O}$, $(\text{R} \cdot \text{H})\text{O} \cdot \text{CO}_2$, $(\text{R} \cdot \text{H})\text{SiF}_6$, $(\text{R} \cdot \text{H})(\text{NO}_2)_2$, $(\text{R} \cdot \text{H})(\text{ClO}_4)_2$, and $(\text{R} \cdot \text{H}_2\text{O})\text{SO}_3\text{H}$. The red salicylatocobaltamine salts described in this paper, when treated with 8 N HNO_3 (5 mols.), dissolved to a dark green soln., whose color was so intense that it was still perceptible at a diln. of 1-part of Co in 6,000,000 of H_2O . "This is one of the most delicate reactions of Co." The various cobaltamines can be converted into hexamine cobaltic chloride by digestion with NH_4OH in the rotating autoclave.

D. MACRAE

Ozone and tautomerism. P. DE PAUW. *Chem. Weekblad* 20, 26(1923).— O_3 should be defined as a dynamic isomeric form of O_2 not as an allotropic form. R. BEUTNER

A convenient method for the preparation of aqueous hydrobromic acid of constant boiling point. J. G. F. DRUCK. *Chem. News* 126, 1(1923).—The procedure recommended by Pickles (cf. *C. A.* 13, 2825) for making concd. aq. HBr was improved in ease of manipulation by adding 10 cc. of concd. H_2SO_4 to 15 g. KBr in 25 cc. H_2O contg. 0.2 g. SnCl_2 , letting stand overnight, decanting and distg. Eighteen cc. of distillate were collected at $120-5^\circ$, contg. 90% of the theoretical HBr with not over 0.07 g. of HCl.

C. C. DAVIS

Studies in gravimetric analysis. XXII. (27) Determination of lead. L. W. WINKLER. *Z. angew. Chem.* **35**, 715-6(1922).—In the presence of Fe, pure PbSO_4 cannot be pptd. from a boiling soln. of low acidity. In a cold soln. a good ppt. of PbSO_4 can be obtained which should be allowed to stand overnight before filtering and should be washed first with 10 cc. of 1% H_2SO_4 . NaNO_3 and NH_4NO_3 do not affect the results seriously but KNO_3 causes high values. The presence of Cu, Zn, Cd, Mg, Al, Mn, Co and Ni in quantities up to 0.35 g. does not affect the results obtained as described in C. A. **17**, 701 and hot pptn. with $(\text{NH}_4)_2\text{SO}_4$ is always preferable except when Fe is present. If a considerable quantity of the above ions is present, however, it is advisable to proceed as follows:—To 25 cc. of soln. contg. 1 cc. of N HNO_3 and the Pb and other cations as nitrates, add 25 cc. of alc. and 5 cc. of 10% $(\text{NH}_4)_2\text{SO}_4$ soln. Allow to stand overnight, filter through a cotton filter, keeping as much as possible of the ppt. back in the beaker. Treat this residue with 10 cc. of 1% H_2SO_4 and heat to boiling. Pour through the filter in 2-3 portions. Collect this part of the filtrate separately, pour it back onto the sulfate residue and heat 15 min. on the water bath. Cool in running water and after 15 min. collect all of the ppt. on the cotton filter, wash with 25 cc. of 50% alc., dry at 130° and weigh the PbSO_4 . The method is suitable for the detn. of Pb in brass or in metallic Zn or Cd. W. T. H.

Conductivity titrations in precipitation analysis. VI. With lithium sulfate for determination of barium, strontium, calcium, and lead. I. M. KOLTHOFF. *Z. anal. Chem.* **62**, 1-7(1923).—Conclusions: (1) Ba salts can be titrated even in very dil. soln. with Li_2SO_4 by cond. measurements. Since the cond. rapidly becomes const. it is necessary to add to the dil. soln. 30% of alc. In the presence of Ca high results are obtained, undoubtedly due to the co-pptn. of CaSO_4 . (2) Sr and Ca cannot be detd. by cond. measurements as the sulfate. (3) The results for 0.05 M Pb soln. were 4% too low, but for 0.01 N soln. in the presence of alc., very good results were obtained. VII. **Barium, strontium, lead, and other metals.** *Ibid* 97-103.—Ba can be titrated in a neutral soln. with chromate. In a weakly acid soln. the results are too high. The presence of Sr gives high results owing to the co-pptn. of SrSO_4 . Sr can be titrated in a 50% alc. soln. with chromate. Pb can also be titrated with chromate. Titration of Ag, Mn, Zn, Cu, and Cd with chromate showed that with the exception of Ag a more or less basic salt was formed, even in 50% alc. soln. These metals, therefore, cannot be detd. by cond. titrations. C. E. CARLSON

An arsenic control test for works laboratories. J. E. BECK. *Chem. Trade J.* **71**, 670(1922).—A description of the Gutzeit test as carried out in an English plant. CdSO_4 soln. is used to activate the Zn. The AsH_3 is passed through narrow tubing, to act as a moisture trap, then through cotton and into a somewhat wider tube contg. $(\text{AcO})_2\text{Pb}$ paper to remove H_2S and finally brought into contact with a disk of HgCl_2 paper. The color produced on this last paper is made more permanent by moistening with 5% KI soln. The standards will then keep a week. The substance tested should not contain more than 0.01 mg. As_2O_3 . W. T. H.

Critic of ozone determinations (a contribution to the problem of gas intoxication in Röntgen rooms). F. LOENNE. *Münch. med. Wochschr.* **68**, 1519-20(1921).—Guthmann claims that gas intoxication of persons in X-ray rooms is not due to HNO_2 or other nitrous compds., but to O_3 . He used the method of Ellwein and Wyl for the detection of O_3 . The hydrochloride of *m*-phenyldiamine is used in NaOH alk. soln. in which HNO_2 and H_2O_2 do not react. But the soln. reacts with air as well as with nitroso compds. in much shorter time than has been thought. There is no doubt that O_3 is present but the quantities have not been detd. satisfactorily. S. AMBERG

Nitrometer method for the determination of nitrogen in nitrates and nitric acid. W. H. WEBB AND M. TAYLOR. *J. Soc. Chem. Ind.* **41**, 362-4T(1922).—The investi-

gation was carried out to det. the cause of the discrepancies often found between the % HNO_3 detd. by the nitrometer and by titration with caustic alkali soln. Conclusions: (1) The N_2 in KNO_3 can be correctly detd. by means of the nitrometer when 91-2% H_2SO_4 is employed and it is assumed that 10 cc. of HNO_3 contain 0.2 cc. of dissolved NO . (2) When HNO_3 is weighed without the loss of fumes, the nitrometer gives values for the % N_2 calcd. as HNO_3 , which agree within 0.15% with the values obtained by titration with alkali. (3) The nitrometer should be used in a room free from rapid fluctuations in temp., and the temp. should be read before the vol. of gas is detd. (4) A large quantity of HNO_3 for analysis should be weighed with a known wt. of strong H_2SO_4 contained in a deep vessel and the necessary amt. of mixed acid weighed into the nitrometer.

C. E. CARLSON

Iodometric determination of arsenic acid. L. M. KOLTHOFF. *Z. anal. Chem.* 62, 137-8(1923).—Dissolve the arsenate in a flask provided with a ground-glass stopper and make the soln. 1 *N* with HCl and the total vol. of soln. 10-30 cc., heat 3 min. on the H_2O bath, add KI , stopper, heat 5-10 min. on the H_2O bath, cool quickly and titrate slowly with $\text{Na}_2\text{S}_2\text{O}_3$. With this procedure the oxidation due to air is negligible because in the preliminary heating most of the air is expelled from the flask. If the arsenate, HCl and KI are mixed at room temp. and then warmed the oxidation due to air is appreciable and with this low acidity the reduction of the arsenic acid is too slow at room temp.

C. E. CARLSON

Characteristics for the evaluation of limestone, dolomite and similar carbonate rocks and a rapid method for analyzing the same. A. DESGRAZ. *Z. angew. Chem.* 35, 714-5(1922).—The attempt is often made to judge a limestone by measuring the vol. of CO_2 evolved on treatment with an acid or by the loss on ignition but these tests often lead to erroneous conclusions. Sometimes an impure MgCO_3 will give the same CO_2 content as a pure CaCO_3 and often substances are present which lose water on ignition. The loss on ignition together with the behavior on slaking gives a better characterization. A pure calcite will give 41-44% loss on ignition, will slake rapidly and give a white oxide. A dolomite will give higher loss on ignition and a more grayish oxide which will not slake as readily. Calcite contaminated with much Fe and Al will show a lower loss on ignition and a yellowish oxide. The following, very rapid method of analysis gives excellent values for CaO and MgO . Dry the sample at 110° and heat 1 g. to const. wt. at $930-950^\circ$ to get the loss on ignition. Slake the residue with a few drops of water and transfer to a 150 cc. beaker. Boil with 30 cc. of a concd. soln. of NH_4Cl until no more NH_3 is evolved; this shows that all of the Ca and Mg has dissolved as chloride. Filter into a 500-cc. calibrated flask, ignite and weigh the residue of Al_2O_3 , Fe_2O_3 , Mn_2O_3 and SiO_2 . In 100 cc. of the soln. det. the Ca by pptn. with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in the usual way. In another 100 cc. of the chloride soln. det. Mg without removing Ca by adding 10 cc. of 10% citric acid soln., 50 cc. of concd. NH_4OH and 30 cc. of 0.5% $(\text{NH}_4)_2\text{HPO}_4$ at 80° . Cool with running water, filter, wash with 2.5% NH_3 soln., ignite and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$.

W. T. H.

Qualitative analysis of the iron group. R. W. HUFFERD. *J. Am. Chem. Soc.* 45, 438-9(1923).—The ppt. produced by $(\text{NH}_4)_2\text{S}$ and NH_4OH in the usual qual. scheme is dissolved in acid and treated with NaOH , exactly as recommended in the textbook of W. A. Noyes, except that a larger excess of NaOH is advised for the sepn. of Al , Cr and Zn from Mn , Fe , Ni and Co . These last 4 elements are detected in the order named by the following well known reactions: Mn by treatment with KClO_4 in HNO_3 soln., Fe by pptn. with excess NH_4OH , Ni by dimethylglyoxime, Co by the Vogel test.

W. T. H.

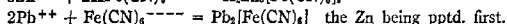
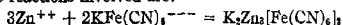
Electrometric determination of cobalt with silver nitrate. E. MÜLLER AND H. LAUTERBACH. *Z. anal. Chem.* 62, 23-8(1923).—The method depends upon the addn.

of an excess of KCN and titration of the excess with AgNO_3 . According to the literature Co forms with an excess of KCN a quadrivalent $\text{Co}(\text{CN})_4$ anion. The ratio of $\text{Co}:\text{CN}=1:5$ was found, however, both in the presence and absence of air. This confirmed the work of Edelman who found Co in an excess of KCN formed a compd. $\text{K}_4\text{Co}(\text{CN})_4\cdot\text{H}_2\text{O}$. Titrations were made with a Ag electrode. In the absence of NH_4OH the results were low but with NH_4OH added the results were excellent. The sudden change in potential was at -0.290 v. in the first case and -0.320 v. in the latter case.

C. E. CARLSON

A method for the quantitative separation of beryllium and uranium. P. H. M.-P. BRINTON AND R. B. ELLSTAD. *J. Am. Chem. Soc.* 45, 395-8(1923).—By adding $(\text{NH}_4)_2\text{CO}_3$ to an acid soln. contg. Be^{++} and UO_2^{++} in the presence of NH_4Cl and $\text{NH}_3\cdot\text{OH}$, HCl , precipitates are formed which dissolve in an excess of $(\text{NH}_4)_2\text{CO}_3$ reagent. By boiling the soln. the greater part of the Be^{++} is pptd. as basic carbonate. In the filtrate the last traces of Be^{++} can be removed as hydroxide by acidifying the soln., boiling off dissolved CO_2 , adding more NH_4OH , HCl and making alk. with NH_4OH . If the last treatment is used to ppt. all of the Be, a very bulky ppt. is obtained which is hard to wash. By igniting the above 2 ppts. pure BeO is obtained. In the filtrate the U may be detd. by pptn. with ammonia as $(\text{NH}_4)_2\text{U}_2\text{O}_7$ after the NH_4OH , HCl has been destroyed by treatment with H_2O_2 , or alkali bromate, in acid soln. It is recommended to ignite the $(\text{NH}_4)_2\text{U}_2\text{O}_7$ to dull redness and weigh as U_2O_5 . W. T. H.

Electrometric titration of zinc and lead in the presence of one another with potassium ferrocyanide. ERICH MÜLLER AND KURT GÄBLER. *Z. anal. Chem.* 62, 29-34 (1923).—The system used was Pt-Hg , HgCl . To every 100 cc. of soln. 1 cc. of $\text{M K}_4\text{Fe}(\text{CN})_6$ was added and the titration carried out with 0.1 $\text{M K}_4\text{Fe}(\text{CN})_6$ at 75° . The reactions involved are:



It is necessary near the first break in potential to wait 3-5 min. before the potential became const. This is probably due to the formation of a little $\text{Pb}_2\text{Fe}(\text{CN})_6$ before all the Zn is pptd. and as a consequence a secondary reaction takes place: $2\text{Pb}_2\text{Fe}(\text{CN})_6 + 3\text{Zn}^{++} + 2\text{K}^{++} = \text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2 + 4\text{Pb}^{++}$. The first break came at $+0.54$ v. and the second at $+0.19$ v. Titrations were performed by setting the potentiometer first at $+0.54$ volts and later at $+0.19$ v. and titrating until the galvanometer passed through the zero reading. For the sum of both metals exact results were obtained but not for Zn alone. Attempts were made with higher temp. (90°) and increasing the K ion concn. but without results. If Pb was pptd. with dil. H_2SO_4 (no great excess) the Zn could easily be detd. Therefore, Zn and Pb can be detd. electrometrically in the presence of one another if 2 titrations are made; one for total Pb and Zn and one for Zn alone.

C. E. CARLSON

A colorimetric method for the determination of small amounts of magnesium. F. S. HAMMETT AND E. T. ADAMS. *J. Biol. Chem.* 54, 565-6(1922).—Sepn. of NH_4MgPO_4 by centrifugation is preferable to filtration because the best acid-washed arabestos, or pulp made from the best grade of filter paper, contains sufficient P, or other substances capable of giving the Bell-Doisy reaction, to yield a well defined colorimetric test. H. and A. have, therefore, modified their procedure (*C. A.* 16, 2342) as follows: the Mg is pptd. in 25 cc. centrifuge tubes, the sides of the tubes are well scratched, and the mixt. is allowed to stand overnight. The ppt. is centrifuged off, washed twice with 10% NH_4OH and once with ammoniacal alc., dried, and dissolved in 10 cc. of 0.1 N HCl in the tube. The detn. is completed as previously described. Carbonate-sulfite solns. not over 2 weeks old should be used and should have been kept in tightly stoppered 500 cc. bottles. Fading of the color which is due to oxidation of the sulfite is thus avoided.

A. P. LOTHROP

The estimation of magnesium in aluminium alloys. W. H. WITHEY. *Chem. News* 126, 17-19(1923).—The procedure is based on the pptn. of Mg as $\text{Mg}(\text{NH}_4)_2\text{PO}_4$ in ammoniacal soln. in which the Fe^{+++} and Al^{+++} are held in soln. by $\text{H}_2\text{C}_2\text{H}_3\text{O}_6$. Zn^{++} , Cu^{++} and Ni^{++} need not be removed, if present in small quantities. For an alloy contg. not more than 1% Mg proceed as follows: Dissolve 2 g. of alloy in 30 cc. of concd. HCl and 10 cc. HNO_3 , add water and filter off SiO_2 . To the filtrate add 15 g. $\text{H}_2\text{C}_2\text{H}_3\text{O}_6$ dissolved in 75 cc. H_2O , and 5 g. NH_4Cl . Make distinctly alkaline with concd. NH_3 , add 25 cc. of a satd. soln. of Na_2HPO_4 , stir and add concd. NH_3 equal to $\frac{1}{3}$ the total vol. of the soln. Allow to stand overnight, filter and wash the ppt. with dil. NH_3 . Dissolve the ppt. in HCl and ppt. again in the presence of 1 cc. satd. Na_2HPO_4 . Allow the soln. to stand for several hrs., filter, wash the ppt. as before and ignite to $\text{Mg}_2\text{P}_2\text{O}_7$. In case the alloy contains Mn, dissolve the ignited ppt. in 6 *N* HNO_3 , treat the soln. with NaBiO_3 , filter and titrate with FeSO_4 . Calc. any Mn thus found as $\text{Mn}_2\text{P}_2\text{O}_7$ and deduct the wt. from the impure phosphate. C. E. CARLSON

The determination of zinc as zinc ammonium phosphate and its use in separations.

II. P. ARTMANN. *Z. anal. Chem.* 62, 8-17(1923).—The best conditions for the pptn. of $\text{Zn}(\text{NH}_4)_2\text{PO}_4$ from a NH_3 soln. are as follows: (1) Neutralize at 60-70° with HNO_3 ; a small excess does no harm if sufficient $(\text{NH}_4)_2\text{HPO}_4$ and 1-2 g. NaOAc are present. (2) Make sure that the concn. of NH_4 ions does not exceed 1 *N* after the addn. of NH_3 and before the addn. of $(\text{NH}_4)_2\text{HPO}_4$. (3) Use 6 times as much $(\text{NH}_4)_2\text{HPO}_4$ as there is Zn present, so that after the complete pptn. the soln. will be at least 0.2 *N* in $(\text{NH}_4)_2\text{HPO}_4$. (4) If $(\text{NH}_4)_2\text{C}_2\text{H}_3\text{O}_6$ (in sepsns.) is added, increase the amt. of $(\text{NH}_4)_2\text{HPO}_4$ so that 3 cc. of 3 *N* $(\text{NH}_4)_2\text{HPO}_4$ soln. is used for every 10 cc. of 2 *N* $(\text{NH}_4)_2\text{C}_2\text{H}_3\text{O}_6$ added. (5) After the pptn. avoid long boiling. To obtain a cryst. ppt. it is sufficient to heat to boiling, with stirring, and allow to remain on the water bath for 20 min. III. The separation of zinc from mercury and nickel. P. ARTMANN AND WALTER HARTMANN. *Ibid* 17-22.—The method recommended for the sepn. of Zn and Hg is as follows: To 100 cc. of dil. HNO_3 soln. contg. 0.1 g. Zn and not more than 0.4 g. Hg, add 6 g. NH_4NO_3 , make ammoniacal with 10-20 cc. 5 *N* NH_3 , add 10 cc. 3 *N* $(\text{NH}_4)_2\text{HPO}_4$, heat to 60° and while stirring neutralize with 5 *N* HNO_3 . Heat to boiling and allow to remain on the water bath for 30 min. Filter through a Gooch crucible and wash the ppt. first with 1% $(\text{NH}_4)_2\text{HPO}_4$ soln. and then with cold water. Dry in the hot closet at 105°. If more Hg or Zn is present, a double pptn. is required. Det. the Hg in the filtrate by the $(\text{NH}_4)_2\text{SO}_4$ method. For the sepn. of Zn and Ni the following conditions are recommended: The pptg. soln., 120-50 cc., should not contain more than 0.1 g. Zn and 0.1 g. Ni. For each 0.1 g. Ni add 30 cc. 2 *N* $(\text{NH}_4)_2\text{C}_2\text{H}_3\text{O}_6$. Before neutralization with 5 *N* HNO_3 or HCl , add 1-2 g. NaOAc . A double pptn. is always required and is carried out as above. The method does not succeed for the sepn. of Zn from Co and Fe. C. E. CARLSON

Combined precipitation and titration method for the determination of copper in alloys. B. WINKLER. *Chem.-Ztg.* 46, 1137(1922).—Dissolve 14 g. of alloy in 30 cc. concd. HCl and 30 cc. HNO_3 added in small portions, warming carefully; dil. with H_2O and transfer to a l. calibrated flask. After thorough shaking pipet off 50 cc. into a 250 cc. beaker, add 50 cc. $\text{NaKC}_2\text{H}_3\text{O}_6$ soln. (170 g. in 500 cc. H_2O) and 25 cc. 4 *N* NaOH , heat to boiling and reduce with an amt. of hydroxylamine (5 g. in 100 cc. H_2O) corresponding to the amt. of Cu present. Boil with care for 1 min. and allow the ppt. to settle. Filter the supernatant liquid through a filter which has been previously covered with a layer of freshly pptd. $\text{Al}(\text{OH})_3$. Wash the ppt. in the beaker by decantation and avoid stirring up the ppt. on the filter. Wash the ppt. on the filter with hot H_2O into a 250 cc. flask. Dissolve the remainder of the ppt. in the beaker and that on the filter in dil. aqua regia and transfer to the flask. Add 10 cc. HNO_3 , HCl , and H_2SO_4 .

and a little KClO_3 and evap. to SO_3 fumes. Add 7 cc. HNO_3 , evap. and finally, after addn. of H_2O and a few cc. strong Br. water, evap. to dryness. Add H_2O and boil, cool, make slightly alk. with NH_3 and then barely acid with H_2SO_4 , add KI and titrate with $\text{Na}_2\text{S}_2\text{O}_3$.

C. E. CARLSON

A new method for the determination of methanol. E. KUHLEFELT AND Y. AIRILA. *Soc. Scient. Fennica-Commentationes Biol.* 1, No. 2, 4 pp.(1922).—Parafuchsin reacts toward HCHO in much the same way as does fuchsin or methyl violet. Since most tests for MeOH depend upon the preliminary formation of HCHO , parafuchsin may be used indirectly as a test for MeOH . Although the bluish red color produced is not strictly proportional to the amt. of MeOH present, the method may be used for the quant. detn. of MeOH provided comparison tests are made at the same time and in the same way with known quantities of MeOH . Parafuchsin has a distinct advantage over fuchsin and methyl violet as clearer solns. are obtained with traces of MeOH and the color developed is more distinct. To carry out the test, place 3 cc. of the alc. in a 50 cc. beaker and add 1 cc. of a soln. obtained by mixing 21 cc. of 95% alc., 40 cc. concd. H_2SO_4 and 200 cc. of water. Then add 1 cc. of 5% KMnO_4 soln., shake once and allow to stand exactly 1 min. Add 1 cc. of 8% oxalic acid soln. and when a brownish yellow color results from the reduced KMnO_4 , clear the soln. with 0.8 cc. of concd. H_2SO_4 . Shake well and when perfectly clear add the parafuchsin reagent which is a satd. aq. soln. which has been decolorized with NaHSO_3 and H_2SO_4 in the usual way.

W. T. H.

A comparison of the most useful methods for the determination of the formaldehyde content of formalin solutions. F. MACH AND R. HERRMANN. *Z. anal. Chem.* 62, 104-37(1923).—Over 30 methods have been proposed since 1896 for the detn. of HCHO , some depending upon a sp. reaction, some upon the formation of addition products and some depending upon oxidation and reduction. There are, however, 4 methods which are specially favored. These are—(1) the H_2O_2 method of Blank and Finkenstein (*Ber.* 31, 2979), (2) the iodometric method of Romijn (*Z. anal. Chem.* 36, 18), (3) the Na sulfite method of G. Lemme (*Chem.-Ztg.* 27, 896) and (4) the NH_3 salt method of C. E. Smith (*Am. J. Pharm.* 1898, 86). In this research these methods were studied with regard to accuracy and to the effect produced by impurities. The H_2O_2 method depends upon the reaction between HCHO and H_2O_2 in a soln. of known alkalinity and the titration of the excess alkali hydroxide. $2\text{HCHO} + \text{H}_2\text{O}_2 + 2\text{NaOH} = 2\text{HCO}_2\text{Na} + 2\text{H}_2\text{O} + \text{H}_2$. Good results were obtained as follows: Take 0.8-1 g. of 30-40% formalin and, if a pipet is to be used, make up a formalin soln. such that this wt. will be contained in not less than 25 cc. Add this soln. to 25 cc. of N NaOH mixed with a few cc. of H_2O_2 soln. Mix immediately by shaking and add more H_2O_2 until 50 cc. of 3% H_2O_2 have been added. If the soln. of formalin is very dil., it is better to use 9% H_2O_2 . After 1 hr. titrate with acid with litmus as indicator. Make a correction for any acidity of the formalin or H_2O_2 soln. Acetaldehyde and acetone appear to be the only impurities likely to be present and affect the results. By the above procedure, the effect of acetone is slight but acetaldehyde tends to retard the reaction with H_2O_2 to a far greater extent and when 8% of acetone is present in formalin, the results are about one-third below the true value. The iodometric method is based upon the oxidation of HCHO to formate in alk. soln. After the reaction is complete the soln. is made acid and the excess I_2 is titrated with $\text{Na}_2\text{S}_2\text{O}_3$. $\text{I}_2 + 3\text{OH}^- + \text{HCHO} \rightarrow \text{HCO}_2^- + 2\text{I}^- + 2\text{H}_2\text{O}$. Take 25 cc. of formalin and djl. to exactly 500 cc. After mixing, transfer exactly 5 cc. to a glass stoppered flask and add 40 cc. of N NaOH all at once and then run in 40 cc. of 0.2 N I_2 soln. from a buret. After 10 min., make acid with 45 cc. of N H_2SO_4 and titrate the excess I_2 with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ soln. Alc., acetone, and MeCHO have a slight effect upon the results, tending to make them a little higher. Polymers

of HCHO are titrated with the H_2O_2 whereas in the H_2O_2 method they have no effect. The NH_4 salt method depends upon the condensation of HCHO with NH_3 , $6\text{HCHO} + 4\text{NH}_3 = \text{N}_4(\text{CH}_2)_6 + 6\text{H}_2\text{O}$. Smith recommended liberating the NH_3 from a neutral NH_4 salt and detd. the excess of NH_3 by acidimetric titration. A series of expts. with this method show that the reactions do not take place quantitatively even with modifications that have been proposed and the results are always a little low. The Na sulfite method depends upon the condensation of aldehyde with sulfite and titration of the liberated alkali with acid. $\text{HCHO} + \text{SO}_3^{--} + \text{H}_2\text{O} = \text{HCH}(\text{OH})\text{SO}_3^- + \text{OH}^-$. Dissolve a weighed portion of formalin in a definite vol. of water so that 25 cc. of the soln. will contain about 3 g. of formalin. Pipet off 25 cc. of this soln. into a wide-mouthed, glass-stoppered flask, add 75 cc. of Na_2SO_3 soln. (0.320 g. per cc.) shake and after 10 mins. titrate with $N \text{ H}_2\text{SO}_4$; rosolic acid is preferably used as indicator. The results agree well with those of the H_2O_2 method but high results are obtained when acetone or MeCHO is present. The conclusion drawn from over 100 expts. is that the H_2O_2 method is the most useful one for the analysis of formalin solns. If a second method is to be used for comparison, the sulfite procedure is recommended because concordant values are obtained with pure HCHO solns. and although the sulfite method is affected more by impurities than is the iodometric method, the fact that higher results are obtained is a valuable indication as they indicate the probable presence of acetaldehyde or acetone which can be tested for qualitatively. A bibliography of over 50 articles is given.

W. T. H.

The determination of hydrocarbons in technical gases. G. WELLERS. *Stahl u. Eisen* 42, 1449(1922).—Acetylene can be detd. in the presence of gases of the ethylene and methane series by absorption in potassium mercuric iodide. The soln. used is 25 g. HgI_2 and 30 g. KI in 100 cc. H_2O . The gases of the ethylene series can be absorbed by a soln. of 1 g. vanadic acid in 199 g. concd. H_2SO_4 . It is not possible to sep. the gases of the ethylene series by treatment with H_2SO_4 of various concns., at room temp. Unsatd. hydrocarbons may be converted relatively easily to satd. ones by passing over Pd satd. with H_2 at room temp. Condensation analysis for hydrocarbons consists of condensing the hydrocarbons by liquid air and then subjecting the condensate to fractional distn.

R. S. DEAN

Residual affinity and coordination (reaction for cobalt) (MORGAN, SMITH) 6. Crucible for the determination of S (HILLER) 1.

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8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

Mineralogy for students of dentistry. E. H. KRAUS. *Am. Mineral.* 7, 203-7 (1922).—Mineralogic methods are of value to dental students in studying the setting of plaster of Paris, dental porcelain, and cements; in identifying the constituents of dental powders; and in recognizing the nature of salts crystg. from saliva. E. T. W.

The colorings of some types of quartz, and their instability. G. O. WILD AND R. E. LIESEGANG. *Centr. Mineral. Geol.* 1922, 481-3.—The idea that color changes in allochromatic minerals, brought about by heat or radiations, is due to changes in the degree of dispersion of coloring particles does not seem possible. The solid structure of crystals would hinder or entirely prevent the aggregation of such particles. Ultra-microscopic examn. of heat-decolorized and natural amethyst afforded no confirmation of the theory of a change in dispersity. E. F. H.

Volume isomorphism in the silicates. E. T. WHERRY. *Am. Mineral.* 8, 1-8 (1923).—In simple compds. with a close-packed crystal structure it is probable that the principal requisite of isomorphous replaceability is that the elements in question must possess approx. equal vols. rather than that they must have equal valencies and be chemically related. There is given a list of mean values for the volumes of atoms of the elements most common in silicate minerals. The theory is applied to certain mineral groups as an explanation of peculiarities of their compn. It explains: (1) in the feldspar group, the limited replaceability of K and Na, and the more complete replaceability of K by Ba; (2) the significance of water in analcite; (3) the lack of K pyroxenes; (4) the presence of alkalis in the beryl group; (5) the excess of SiO_2 in the nephelite group; (6) the extensive isomorphism in the garnet group; (7) the homology of melonite and marialite and the entrance of CO_2 and SO_2 groups; (8) the possibility of replacement of Li for Fe'' and Al for Mg in tourmaline; (9) the non-existence of (Ca, Na) and (SiO_4 , Si_2O_6) replacements in the zeolite group; (10) the absence of (SiO_4 , Si_2O_6) replacement in the micas. E. F. H.

Note on leuchtenbergite from Philipsburg, Montana. E. V. SHANNON. *Am. Mineral.* 8, 8-10 (1923).—Well developed tabular hexagonal crystals of leuchtenbergite were collected near Lost Creek, Philipsburg district, Mont. The mineral is associated with calcite and wollastonite in a marble. It is colorless to pale talc green; $H=3.5$. The optical properties (C. S. Ross) are: biaxial, +, $2V=6-14^\circ$, $\alpha=\beta=1.572$, $\gamma=1.575$. Analysis gave: SiO_2 31.44, Al_2O_3 17.62, Fe_2O_3 none, MgO 37.64, CaO , FeO , MnO traces, $\text{H}_2\text{O}+13.19$, sum 99.89%. This leads to the usual formula: $5\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 4\text{H}_2\text{O}$. E. F. H.

Nephrite celt from Bahia, Brazil. H. S. WASHINGTON. *Pan-American Geologist* 37, 198-202 (1922).—The celt was found near Rio Paraguassu, Bahia, and is a slightly yellowish green in color, translucent, tough, with $H=\text{about } 6.5$, and sp. gr. = 2.9382. The ns. were $\alpha=1.597$, $\gamma=1.625$ (Merwin). Analysis gave: SiO_2 59.79, TiO_2 0.23, Al_2O_3 0.88, Cr_2O_3 none, Fe oxides 1.29, MnO 0.10, MgO 24.31, CaO 12.52,

Na₂O 0.35, K₂O 0.06, H₂O 2.10, P₂O₅ none, sum 99.95%, thus indicating a very pure tremolite. S. G. GORDON

The geology of Anglesey. F. GREENLY. *Mem. Geol. Survey, Gt. Britain* 1919, pt. 2; *Mineralog. Mag.* 19, 342(1922).—A glockerite contg. 8H₂O:1SO₃ is described and named *hydroglockerite*. E. T. W.

Notes and analyses of the Hermitage Plains aerolite. H. P. WHITE. *Rec. Geol. Survey, New South Wales* 9, 108-9(1920).—The analysis gave: H₂O (100°) 0.43, H₂O (above 100°) 1.31, SiO₂ 37.96, Al₂O₃ 2.95, MgO 24.87, CaO 2.86, Na₂O 0.97, K₂O 0.21, Fe 19.19, Ni 2.06, Co 0.08, CO₂ 0.10, SO₃ less than 0.01, Cl less than 0.01, P 0.10, FeS 4.05, Cr₂O₃ 0.29, MnO 0.16, V₂O₅ less than 0.01, O by diff. 2.41, sum 100%. BaO, SrO, Li₂O, ZrO₂, TiO₂, and Cu were absent. S. G. GORDON

Development of chemical and metallurgical industries in Canada. A. W. G. WILSON. Can. Dept. Mines, *Summary Report No. 574*, 5-8(1922).—The economic situation is discussed showing that Canada imports over 300 million dollars worth of minerals and manufactured mine products, a large portion of which could be produced within her own borders. **Titaniferous ore deposits.** A. H. A. ROBINSON. *Ibid* 8-10.—Deposits contg. more than 2% Ti are with one exception found in Quebec and Ontario provinces. These deposits show the usual characteristics of such ores but have not yet been explored sufficiently to est. their quantity. **Mineral pigments in Eastern Canada.** H. FRÉCHETTE. *Ibid* 11, 13.—The most important com. sources of ocher are in Saguenay Co. on tide water of the Petite Romaine river. This ocher is being used as a pigment in paper making and a plant is being constructed to grind and calcine the ocher for paint. Some 20 occurrences in Nova Scotia were visited but the deposits were too small to be of com. value. In Alberta Co., N. B., a mine was formerly worked for ferromanganese. This ore contains 22.79% Mn and 15.89 Fe. When ground in oil before calcining it yields a raw umber pigment, after calcining a burnt umber pigment. Both products are more reddish in tint than the usual raw and burnt umber. **Alkali deposits of Western Canada.** L. H. COLE. *Ibid* 16-9.—Sol. mineral salts are found in the provinces west of Ontario, and consist either of solid salts and brines in basins or brines of flowing streams or springs. These salts consist of mixts. of Na and Mg sulfates with generally small amts. of NaCl. Nearly all of these salts used in Canada are imported. **Bituminous sands of Alberta.** S. C. ELLS. *Ibid* 19-22.—Methods for prospecting and testing the sands are given. The factors which chiefly control com. development are thickness and character of the overburden; conditions controlling wasting of the overburden, are quality and quantity of sand, and transportation facilities. **Ores tested.** W. B. TIMM AND R. K. CARNOGHAN. *Ibid* 23-38.—Assays or analyses of 2 graphite, 2 Cu, 3 Au, and 1 each of Mo, Sn, Pb-Zn magnesite and celestite samples are reported in detail with advice as to the best methods for handling the ores.

L. W. RIGGS

The Mattawin iron range. F. HILL. *Iron Steel (Can.)* 6, 12-6(1923).—The Mattawin magnetite range is 50 m. west of Port Arthur, on the C.N.R.R. The deposit is 1400' X 3 mi., and estd. as over 5000 ft. in depth. The ore is (1) banded with jasper, Fe content 35-45%; (2) intimately mixed with SiO₂, Fe 30-8%. A number of analyses are given. E. F. H.

Secondary sulfide enrichment exhibited by certain auriferous veins. P. C. WHITEHEAD. *Bull. Inst. Mining Met.* 219, 8 pp.(1922); *Discussion. Ibid* 220, 11 pp.(1923).—The area described is a spur of a subsidiary mountain chain between the Atlantic and main Cordilleras, in southern S. America. Outcrops at high elevations show superficial enrichment due to surface concn. of the Au, not entirely removed by soln. from primary Fe sulfides. Next is a zone leached of Au, followed by an enriched zone.

E. F. H.

An important mineral deposit in the region of Villacidro, Sardinia. EDOARDO SANNA. *Rass. min. met. chim.* 57, 63-7(1922).—An important source of galena is described near Villacidro, Sardinia, in Silurian schist, covering an area of 400 hectares. The deposits are richest in galena in proximity to their contact with granite, and where the veins intersect at acute angles. For each mass rich in mineral, there is a vein, at times 100 m. in length, composed of 3 sections which divide and reunite, at least one of them contg. galena. The richest veins are those in the vicinity of the Macciurru deposits already described (cf. C. A. 16, 2284). Development by grinding and flotation is recommended. It is estd. that 1,742,000 kg. of com. galena can be extd. together with 175,000 kg. already available for treatment. C. C. DAVIS

Veins of ore at S'Acqua Bona, Sardinia. SALVATORE FOIS. *Rass. min. met. chim.* 57, 69-71(1922).—Veins of various ores not yet exploited at S'Acqua Bona are described. They are apparently of Silurian age and contain limestone and calcareous schists identical with those of Perdas de Foga and Zoppi, as well as black and ordinary yellowish micaceous schists. The schists contg. the minerals surround the granite plateau of Arburese, whereas other schists with metamorphic limestone, quartz and hornfels form an enormous crest approx. 800 m. long parallel to the granite contact. In the different veins are galena, cerussite, limonite, sphalerite, pyromorphite, pyrite, etc., in some cases in ams. insuring successful exploitation. The geologic features of the individual veins are described in detail. C. C. DAVIS

Mass distribution in the interior of the earth compared with the structure of certain meteorites. V. M. GOLDSCHMIDT. *Naturwissenschaften* 10, 1014(1922).—A correction (cf. C. A. 17, 518). C. C. DAVIS

Talc and soapstone in Canada. H. S. SPENCE. Can. Dept. Mines, *Mines Branch* No. 583, 85 pp.(1922).—Practically the entire output of Canadian talc in recent years has been derived from 3 mines and mills in the Madoc district, Hastings Co., Ontario. Soapstone consumed by Canadian kraft paper mills is imported from the U. S. Chem. analyses, mostly by A. Sadler, of 56 samples of Canadian talc or soapstone and 4 U. S. samples are listed. Production, exports, imports, consumption in various industries and prices of talc both for Canada and the U. S. are given. Mines and occurrences in B. C., N. S., Ont. and Que. are described. Talc, steatite and soapstone are distinguished and the process of milling talc is described at length with frequent references to the work of the U. S. Bureau of Mines and Geol. Survey. L. W. RIGGS

Colombian oil fields. L. G. HUNTLEY AND S. MASON. *Trans. Am. Inst. Min. Met. Eng.* No. 1189, 9 pp.(1922).—The geography and geologic structure with special reference to the com. possibilities for the production of petroleum together with the present rate of taxes on production are fully given. The oil-bearing sediments giving the greatest promise for oil production belong to the Tertiary and occur to an important extent along the eastern cordillera including the Magdalena Valley and also in a more recent coastal uplift from Barraquilla to the gulf of Uraba. A high grade of oil is said to be produced from the Magdalena Valley but the quantity is not given. E. T. ERICSON

A petroleum field intelligently developed. ELPIDIO PAPARELLA. *Rass. min. met. chim.* 57, 57-63(1922).—A description of the methods employed in extg. oil from the Wietze wells, Hannover, Germany, supplemented by a survey of the geological relations between saline deposits and petroleum in various countries. C. C. DAVIS

Geologic reconnaissance of the Pidatan oil field, Cotabato Province, Mindanao. W. D. SMITH. *Philippine J. Sci.* 20, 23-42(1922).—The principal formations of the district are Tertiary sediments, intruded at the edge of the field by basalts and andesites. The geologic conditions for oil in the Pidatan oil seep are regarded as unfavorable, but there is a possibility of locating oil structures in the nearby regions of central Mindanao. S. G. GORDON

The occurrence of bitumen in Bombay Island. C. S. FOX. *Rec. Geol. Survey India* 54, 117-28(1922).—The bitumen occurs on the floor of cavities measuring up to $20 \times 30 \times 8$ feet, in a greenish dolerite. The sides and roof of the cavities, and the surface of the bitumen on the floor are encrusted with crystals of calcite, quartz, and zeolites. A description and analysis of the pitch from one of the cavities are given, as well as two analyses of basalt from other localities on the island. The source of the hydrocarbon is believed to have been the sedimentary beds into which the dolerite sill was intruded.

S. G. GORDON

The genesis of melillite. N. L. BOWEN. *J. Wash. Acad. Sci.* 13, 1-4(1923); cf. *C. A.* 15, 3436.—Monticellite occurs in alnoitic rocks from Polzen, Bohemia. (Called to B.'s attention by K. H. Scheumann.) Analcite occurs as a residual mineral in some melillite rocks. At depths the reaction between nephelite and pyroxene to produce analcite and melillite is reversed. Interaction of nephelite and pyroxene with rapid cooling to prevent reversal at lower temps. is probably responsible for the formation of most melillite.

E. F. H.

Investigations of magmatic systems of many components. I. II. W. ERTEL. *Neues Jahrb. Mineral. Geol. Beil.-Bd.* 44, 369-401; 45, 275-310(1921).—(I). This paper takes up graphic methods for representing the compn. and properties of poly-component systems. (II). The methods of the first paper are applied to magmatic systems. They contain 9 principal components: SiO_2 , $[\text{Al}, (\text{Cr})]_2\text{O}_3$, $[\text{Fe}, (\text{Mn})]_2\text{O}_3$, $[\text{Fe}, (\text{Mn}, \text{Ni}, \text{Co})]_2\text{O}_3$, $[\text{Mg}, (\text{Be})]_2\text{O}_3$, $[\text{Ca}, (\text{Sr}, \text{Ba})]_2\text{O}_3$, $[\text{Na}, (\text{Li})]_2\text{O}$, $[\text{K}, (\text{Rb})]_2\text{O}$, and $\text{H}_2\text{O}(\text{F}, \text{Cl})$. The minerals of magmatic rocks represent non-variant points of the system. Mixed crystals are next discussed. The analyses of abyssal members of the normal and alkaline granite families are plotted, and their position on the diagrams is studied with special reference to the mineral compn. of such rocks.

E. F. H.

Genesis of anorthosites of Piedmont, Pennsylvania. ISABEL F. SMITH. *Pan-American Geologist* 38, 29-50(1922).—A small mass of anorthosite occurring near Honeybrook, Chester Co., Pa., is described. An analysis of the anorthosite, and one of quartz-monzonite from the vicinity, are given.

S. G. GORDON

The norite of Sierra Leone. F. DIXEY. *Quart. J. Geol. Soc.* 78, 299-347(1922).—The norite of the Sierra Leone is a stock, 24 miles long and 8 miles wide, which, with the narrow coastal plain of Pleistocene sediments, makes up the peninsula. The contact with the older rocks is obscured by these sediments. The first intrusion of norite, consisting of Labradorite, augite, and hypersthene with varying amts. of olivine and titanomagnetite, was followed by coarser norites, norite pegmatite, beerbachite, norite aplite, and dolomite. The older norite shows flow banding. An interesting series of binary and ternary intergrowths of the minerals of the norite was observed, indicating the importance of eutectic conditions during crystn. The older norite was subjected to varying degrees of metamorphism by the younger members of the complex. An analysis of the older norite showed: SiO_2 48.25, Al_2O_3 21.54, Fe_2O_3 3.59, FeO 3.60, MnO 0.45, CaO 9.73, MgO 6.80, K_2O 1.60, Na_2O 1.76, P_2O_5 0.015, TiO_2 0.26, H_2O above 105° 2.90, sum 99.99. Petrographic descriptions of the rocks, with a discussion of the order of crystn. of the minerals, are given.

S. G. GORDON

A composite sill of Newton Abbot (Devon). W. G. ST. J. SHANNON. *Quart. J. Geol. Soc.* 78, 311(1922).—A composite sill of dolerite, picrite, and mugearite is described, with Rosiwal mineral compns.

S. G. GORDON

Xenolithic tertiary minor intrusions in the Island of Mull, Argyllshire. H. H. THOMAS. *Chemical analyses.* E. G. RADLEY. *Quart. J. Geol. Soc.* 78, 229-60(1922).—The xenoliths in the minor tholeiitic and andesitic intrusions of western Mull are of both cognate and accidental character, and the latter of both siliceous and aluminous types. The siliceous xenoliths show quartz grains with fringes of tridymite, and in

some cases of augite. The aluminous xenoliths are characterized by such minerals as corundum (sapphire), spinel, sillimanite, cordierite, and anorthite. The minerals of the xenoliths, their mode of formation and mutual relations, and the conditions and course of metamorphism are described.

S. G. GORDON

Ordovician lavas of the Mynydd Prescelly, N. Pembrokehire. G. M. PART. *Geol. Mag.* 59, 310-23(1922).—The lavas comprise soda-rhyolites and felsites, sodatrachytes, and keratophyre, of which petrographic descriptions and analyses are given.

S. G. GORDON

Some points in sedimentary petrography. R. H. RASTALL. *Geol. Mag.* 60, 32-9 (1923).—A discussion of the panning and economy of heavy liquids, grading of material, dark ground illumination, and the primary sources of heavy minerals.

S. G. G.

Banded precipitates of vivianite in a Saskatchewan fireclay. J. STANSFIELD. *Geol. Mag.* 59, 356-8(1922).—The vivianite (Fe⁺⁺ phosphate) occurs as bluish black stains, of spherical to elliptical form, on a light gray fireclay, at Clayback, Sask., Canada. They show a banded structure.

S. G. GORDON

Oil shales in eastern European Russia (MÜHLEN) 22. The black quartz of the radium-bearing mine of Viaris (BENSAUDE, COSTANZO) 3. Some ferruginous concretions (STEEL) 11A. High-grade clays of the eastern United States with notes on some western clays (RIBS, *et al.*) 19. Clays (BOUDOUARD, LEFRANC) 19.

COLR, GRENVILLE A. J.: Rocks and their Origins. 2nd Ed. Cambridge: The University Press. 175 pp. 4s. Reviewed in *Nature* 110, 768(1922).

FORD, W. E.: Dana's Textbook of Mineralogy. 3rd Ed. Enlarged. New York: John Wiley and Sons, Inc. 720 pp. 31s. 6d. in Australia. Reviewed in *Chem. Eng. Mining Rev.* 15, 137(1922).

GRABAU, AMADEUS W.: Geology of Non-Metallic Mineral Deposits other than Silicates. Vol. I. Principles of Salt Deposition. New York: The McGraw-Hill Book Co., Inc. 435 pp. Reviewed in *Science Progress* 17, 493(1923).

MATZNER, J.: Chemia a mineralogia pre stordú triedu gym. Pomoci: J. Petrovici and V. Petroviča. 143 pp. Kč 17.60.

WYER, SAMUEL S.: Smithsonian Institution's Study of Natural Resources Applied to Pennsylvania's Resources. Washington: Smithsonian Inst. 150 pp. Reviewed in *Chem. Met. Eng.* 28, 130(1923).

9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, R. S. WILLIAMS

Herman Hubert. ANON. *Rev. universelle mines* 15, No. 3, I-IV(1922).—An obituary with portrait.

C. C. DAVIS

The work of the metallurgical inspectorate, Government of India. R. MATHER. *J. Indian Ind. Labour* 2, 462-72(1922).—A description of equipment as well as work.

A. P.-COUTURE

Recent developments in the treatment of oxidized copper ores. WILTON SHELL-SHEAR. *Chem. Eng. Mining Rev.* 15, 67-9(1922).—Successful commercial methods, and promising new methods are reviewed, more particularly those being carried on in America. Both flotation and leaching methods and treatment of ore and soln. after leaching are discussed. There is no one method suitable for all types. The electrolytic process has many advantages where large tonnages are available, especially for ores having low Fe in soln. after leaching. Costs can be reduced by leaching with H₂SO₄ obtained from roasting sulfides. Where only limited tonnage is available the production

of sponge Fe on large scale at low cost will facilitate cheap treatment of many ores. New inventions are needed especially in the field of ores with high calcite and other acid-consuming constituents.

Chemical methods of iron ore purification. A. J. MOXHAM. *Iron Age* 111, 31-2 (1923).—The ore is leached with H_2SO_4 , with recovery of the acid, and calcined with Na_2CO_3 , with recovery of the Na_2CO_3 . A small operative plant is now being built in Delaware.

H. C. PARISH

Possibilities of dry chlorination of oxidized zinc materials. C. G. MAIER. *Eng. Mining J. Press* 115, 51-4(1923).—Small-scale expts. indicate that Cl gas can replace O in oxidized zinc-bearing ore without the use of reducing agents. High-grade $ZnCl_2$ might be made on a com. scale.

H. C. PARISH

The calcination of calamine fines by means of exhaust from explosion motors. LOUIS TISSIER. *Chimie et industrie* 8, 1201-5(1922); cf. U. S. pat. 1,364,656(C. A. 15, 717).—T. discusses the application of his process to the calcination of $ZnCO_3$ fines to ZnO. The exhaust, at about 450° , is discharged into a special oven contg. calamine fines. In certain cases it is advisable to add 0.5-1.5% of wood charcoal (exceptionally up to 3%). Blowing air through the charge greatly hastens the rate of the reaction. The temp. rises to about 650° , owing to oxidation of the H₂ and CO of the exhaust gases. Calcination by this process is sure; there is no danger of excessive temp. or of jams forming. There are no unburnt portions, and the quality of the ZnO is not lowered by ash from the fuel, as in the usual processes (4-12% fuel added). The cost of the oven is negligible, and the cost of operation about 20% that of ordinary processes. Using the exhaust in this manner does not affect the power delivered by the motor. The process has been found suitable for the *manuf. of plaster*, and for the *roasting of blende ores*. Complete roasting of an ore contg. 20% S was obtained without addn. of any fuel, the roasted product being free from sulfates and contg. 1% S. The roasting temp. never exceeded 700° . The roasting effect is due to the presence of O₂ (about 8%) in the exhaust gases, and the absence of sulfates to the presence of considerable amts. of CO₂.

A. P.-C.

Blast roasting of silver-lead ores. P. J. WALSH. *Chem. Eng. Mining Rev.* 15, 55-61(1922).—The plant consists of (1) Dwight-Lloyd blast roasting machines operated solely as a pre-roasting unit, (2) D.-L. machines operating to full capacity as a final roasting unit, treating the main portion of pre-roasted material, and (3) Huntington-Heberlein pots operating as a final roasting unit and treating the part of pre-roasted material which (2) is unable to handle. Analyses and sizing tests of ores, fluxes, etc., are discussed and the process is described.

H. C. PARISH

Offers simple test for sand. E. W. SMITH. *Foundry* 41, 34-5(1923).—S. det. the fraction of bond and of silica by vibration of the sample covered with water in a glass bottle, the two, after sufficient treatment, being found divided by a distinct line, and the proportion of each is detd. by means of a pocket rule.

S. L. CHISHOLM

Compares cupola receivers. F. J. COOK. *Foundry* 51, 27-30(1923).—A tech. discussion of the advantages of several types.

S. L. CHISHOLM

Plans test to define sands. I. R. J. DOTY. *Foundry* 51, 15-8(1923).—In expts. made to develop a standard method of foundry sand testing it has been found that measurement of length or wt. broken from a bar pushed over the edge of a plate is impractical. Horizontal tension methods in general are unreliable and vertical tension methods are less concordant than transverse tests. Attempt has been made to refine the latter type of test with fair results.

S. L. CHISHOLM

The resistance of materials—Characteristic properties of soft steel previously hardened by traction. J. SEIGLE. *Compt. rend.* 175, 484-6(1922).—Similar tests on soft steel before and after hardening by traction show no change in tensile strength

or type of fracture, a 100% increase in elastic limit in tension and in torsion, a 50% increase in resistance to fatigue, a less impact angle in smooth bar shock tests, and a 60% decrease in Charpy notched bar tests. *Ibid* 571-2.—Although the Charpy values are low they are higher than rail steel, duralumin and cast Fe. This, together with the high elastic limit, offers a possibility of substitution. 2.5% Ni-steels may be given a very high elastic limit by this treatment.

W. A. MUDGE

Control of sulfur in the basic open-hearth steel process. S. V. WILLIAMS. *Blast Furnace Steel Plant* 11, 51-4 (1923).—The sources of S in open-hearth steel, (pig iron, scrap, fuel and fluxes), are considered and means for limiting the amt. in each are stated. Methods of preventing absorption of S from the fuel and of removing it from the melted bath are reviewed. Pig iron should contain 1-2% Mn, if S removal is to proceed to the expected degree (0.07% approx.) by the time the melted Fe leaves the "mixer." The Saniter CaCl_2 process in which CaO and CaCl_2 are used together may be applied in the "mixer" but is more often used in the open-hearth furnace ladle. CaCl_2 9 and CaO 1 part will remove all but a trace of S. Fifty to 60 lbs. of a mixt. of equal parts CaCl_2 and CaO per ton of steel will if added in small successive portions to the metal in the ladle reduce the S below 0.03%. Scrap should be sprayed with a fire-clay wash to hinder S absorption when CO liberates it from SO_2 or H_2S . In the open-hearth furnace the slag should contain 50-60% CaO and the bath should be circulated so that the slag may perform its function of reducing the S to 0.04% or less. Mn must be present in amt. sufficient to prevent Fe from recombining with S. Addn. of 0.6-0.7% Mn in recarburizing reduces S by 0.01%. Addn. of CaC_2 in the ladle is helpful. The Saniter process may be used in the furnace as well as in the ladle. The extent of its use is not stated. W.'s practice is based on the use of CaO and of Fe-Mn.

J. O. HANDY

The Fiechtl vertical retort furnace for zinc ores. W. KAPPELLMANN. *Eng. Mining J. Press* 114, 1153-4 (1922).—The new furnace has great advantages over the old type from the standpoint of simplicity of design, cost of erection and operation. A saving of $\frac{1}{3}$ the no. of retorts per furnace, a 70% reduction in labor cost, 40% installation cost and 27% fuel cost is claimed over the old type.

H. C. PARISH

Use of liquid fuel in metallurgical furnaces. R. C. HELM. *Blast Furnace and Steel Plant* 10, 549-56 (1922).—The use of fuel oil and tar with a discussion of various types of burners is given. The successful use of fuel oil depends on furnace design, proper methods of distribution and on burners which will thoroughly atomize the fuel. For future development mechanical injection of the oil and the use of the recuperative principle for the gas must be perfected. The discussion is mainly devoted to open-hearth furnaces and to furnaces for the heat treatment of wire products.

C. H. HERTY, JR.

Powdered coal for malleable. II. T. W. ATTERBURY. *Foundry* 50, 880-4 (1922); cf. C. A. 17, 255.—With a 25-ton air furnace burning powdered coal a gas velocity of 31 ft. per sec. was obtained in the furnace. The coal consumption was 40 lb. per min. and a fan with a capacity of 8500 cu. ft. of free air per min. met all requirements. The coal rate should also be 3 to 4 lb. per cu. ft. of total furnace vol. The application of powdered coal to annealing ovens is considered, the advantages of powdered coal firing are briefly reviewed and equipment for the prepn. of the coal is discussed.

C. H. HERTY, JR.

Flue dust briquetting by the corrosion process. A. L. STILLMAN. *Iron Age* 110, 1571-2 (1922).—The corrosion process consists of mixing copperas 1, water 9, fresh flue dust 45, and old flue dust 45 parts, masticating the mix and pressing out the briquets. The app. used is described.

C. H. HERTY, JR.

Notes on the thermal balance of the cupola. J. SEIGLE. *Rev. metal.* 19, 406-15

(1923).—Practical experiences in operating the Fe cupola with special emphasis upon the influence of design, compn., wt. of charge, gas analyses and temp. Many data are given in several tables and formulas. W. A. MUDOG.

Use of magnetic ore in the blast furnace. G. P. PRILLING. *Trans. Am. Inst. Mining Met. Eng.* No. 1199-S, 13 pp. (1922).—Magnetic ores are classified as fine unsintered ore, raw lumpy ore, and fine ore that has been sintered. The least desirable is the lumpy or coarse ore. The raw fine ore is better. The operating difficulties with the fine unsintered ore are very great. The sintered fine ores are by far the best of the three for the blast furnace. Sintering does away with furnace trouble and irregularity almost entirely. S is very low and it is possible to run uniformly high acids in the slag. As none of these ores contains any appreciable amt. of Mn it is necessary to add Mn as high-Mn ore, or the cinder from a furnace running on Fe-Mn. The successful use of magnetic ores is dependent on correct furnace design, stock distribution, rate of driving, air distribution, flux, selection of coke. The coke consumption averages 2250-2500 lb. per ton of pig (Si 1.75-2.75%) and 2000-2100 lb. for Si under 1.00%, when fine unsintered ore is used. With sintered ore the coke consumption is 1832 lb. per ton of pig. Also in *Blast Furnace Steel Plant* 11, 148-52 (1923). C. H. HERTY, JR.

The influence of overheating of, drying of, and addition of oxygen to, the blast of blast furnaces. DERCLAY. *Rev. univ. mines*, Oct. 1, 1922; *Technique moderne* 14, 622-3 (1922).—A general discussion. A. P.-C.

Operation of small converters with lateral blast. LEVOZ. *Technique moderne* 15, 30-1 (1923).—A detailed description of the most satisfactory method of operation. A. P.-C.

The desulfurization of metals by lime. B. BOGRTCH. *Compt. rend.* 176, 103-5 (1923).—Studying the distribution coeff. of S between metals and slags, B. melted 100-g. lots of Fe, Ni, and Mn with S in a graphite crucible at 1500-1600° in a resistance furnace. 20 g. of the desulfurizer (lime, calcareous slag, or lime and fluospar) were added and stirred with a carbon rod. The metal and slag were sepd. and analyzed. Slags are capable of absorbing S up to about 22% of S. At 1500-1600° such slags are almost solid. There still remains a small amt. of free lime, uncombined with S, but with increasing amts. of CaF₂ the absorption of S increases until all the lime is transformed into sulfide. With Fe the slag may contain 500 times as much S as the metal; with Ni and Cu as high as 2000 times; with Mn less than with Fe. Pure metals can be prepd. by this method directly from the sulfides without roasting or reduction.

M. O. LAMAR

Colloidal chemistry and metallurgy. H. MEYER. *Kolloid Z.* 31, 310-3 (1922).—The system Fe-iron carbide is of very great importance. If the dispersion is of colloidal dimensions, many characteristics and properties of the various sorts of steel can be explained.

A. MUTSCHELLER

Cored crystals and metallic compounds. E. C. BAIN. *Chem. Met. Eng.* 28, 65-9 (1923).—Each cored dendrite contains many small crystals with similar lattices but slightly differing in compn. and dimension. Intermetallic compds. usually have complex lattices, giving little opportunity for slip, and hence are brittle. V. O. HOMERBERG

White metals. WM. A. COWAN. *Ind. Eng. Chem.* 15, 29-31 (1923).—A general discussion is given on bearing metals, solder and type metals. V. O. HOMERBERG

Effect of temperature, pressure and structure on mechanical properties of metal. ZAY JEFFRIES AND R. S. ARCHER. *Chem. Met. Eng.* 27, 747-51 (1922).—Recrystall., annealing, cold-work and inclusions have a profound effect on size and shape of cryst. grains and therefore on properties of metal. A discussion is given of the mech. properties of single crystals. V. O. HOMERBERG

Hot working of metals. R. GENDERS. *Bull. Brit. Non-Ferrous Metals Res.*

Assoc. No. 7, 7-11(1922).—Hot-working is defined as mechanical treatment at a temp. above that at which recrystn. takes place rapidly. The proper working temps. of a number of brasses are given. The extrusion process is considered. V. O. H.

Merchant bar iron made by the busheling scrap process. W. M. MYERS. *Proc. Am. Soc. Testing Materials* 22, Pt. II, 187-92(1922).—M. defines and distinguishes the wrought iron made by the busheling process from puddled iron and from steel. The A.S.T.M. defines the busheling process as "heating to a welding heat in a reverberatory furnace, miscellaneous iron, steel or a mixt. of iron and steel scrap cut into small pieces." Merchant bar iron is wrought iron made by that process. About $\frac{2}{3}$ of all wrought iron is thus made while the rest is made by the puddling process. Busheling furnaces may have either "cinder" or "sand" bottom. When the former is used the process resembles puddling, especially when cast iron borings are added to the charge. The "Ely" and the "Sellers" are mechanical busheling furnaces which are apparently successful. Physical tests of the product from 5 different mills show yield point 32500-39500 lb. per sq. in., tensile strength 47000-52000, elongation in 8 in. 28 to 32%, reduction of area 46-59%. Chemical analyses showed C 0.02-0.106, Mn 0.10-0.57, P 0.019-0.064, S 0.022-0.055, Si 0.038-0.315%. The physical tests are higher than those of puddled wrought iron. The Mn is higher and the P lower than in puddled iron. If good low-C scrap is used and is well worked the merchant bar will be practically equal to puddled iron. If high-C scrap or alloy steel is used, poorly welded spots result.

JAMES O. HANDY

Wrought iron. H. E. SMITH, et al. *Proc. Am. Soc. Testing Mat.* 22, Pt. I, 131-3 (1922).—Proposed revisions of standards and tentative standards are enumerated.

V. O. HOMERBERG

Some observations on the "nick-bend" test for wrought iron. H. S. RAWDON AND SAMUEL EPSTEIN. *Proc. Am. Soc. Testing Materials* 22, II, 193-216(1922).—The investigation consisted of the fracturing, under known conditions, of nicked bars of a number of grades of wrought Fe, the comp., mech. properties and structure of which had been carefully detd. The material in most cases had been manufd. to meet certain A.S.T.M. specifications. Nicked bars, representative of the different materials furnished by various manufacturers, were broken under different conditions varying from a simple transverse bending of a specimen supported at the ends to a severe single-blow impact test (drop test). The appearance and nature of the fracture produced under these different methods of fracturing were the features that received most attention.

V. O. HOMERBERG

Proposed revisions in standards for steel. ANON. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 78-80(1922).

V. O. HOMERBERG

Continued discussion on the physics of steel. WM. R. WEBSTER. *Trans. Am. Inst. Mining Met. Eng.* 1205-S, 6 pp.(1923).—Curves show the av. results of tests on $\frac{3}{4}$ -in round bars, varying in C and Mn contents, rolled from test ingots of acid Bessemer steel and basic open-hearth steel.

V. O. HOMERBERG

The brittleness of steel and single shock tests on notched bars. HENRI POMMERENKE. *Rev. métal.* 19, 741-7(1922).—The results of numerous tests are described. With steels having a high resiliency, the Charpy and U. F. test bars give results of the same order, and practically half of those obtained by the Mesnager; so that there does not appear to be any advantage in introducing a new type of bar after adoption of the Charpy bar by the 1909 and 1912 Congresses as international standard. With steels having a high or medium resiliency, the small Frémy bars (30 mm.), tested on a Guillery tester, give as valuable results as the 55-mm. bars tested in the Charpy tester, and have the advantage of much smaller vol. The simultaneous use of bars with round or square notches, and of bars with wedge-shaped notches gives the shock resistance of the steel as abs. brittleness, intermediate brittleness, and abs. shock resistance. This classifica-

tion is valuable (as shown by the behavior of the pieces under working conditions), apart from the resiliency indicated by each bar. The Fremont-Guillery test is particularly advisable for this classification of brittleness. A. P.-C.

A new form of test bar for the notched-bar shock test. SANITER AND BAKER. *Rev. metal.* 19, 633-5(Abs.)(1922).—According to Hadfield low-C steels can be classified either as ductile or as brittle, depending on the rate of the shock; according to Stanton contradictory results can be obtained with the same steel depending on the section of the test-bar. In mild steels the shape of the bar at present in use involves considerable deformation and incomplete rupture. In order to overcome these drawbacks, S. and B. devised a bar notched on 3 sides, having the same useful cross-section as the usual bar. The same thickness and same notch are used as on the standard British Engineering Assn. bar, but the width is increased to allow for the two side notches which are the same as the front notch. Tests were carried out with a Charpy pendulum. The results show that the deformation of the broken bars is reduced to a min., and that the energy absorbed is lower than that in the standard test. The velocity of the shock was 5.1 m. per sec.; but as there is little or no deformation the results obtained are similar to those generally obtained with much higher velocities. In steels with high brittleness, the brittleness found is higher with thick bars than with thin ones; and similarly with steels with low brittleness it is lower with thick bars; this explains why comparable results cannot be obtained with bars of different dimensions (either standard or proposed bar). A. P.-C.

Structure of martensitic carbon steels and changes in microstructure which occur upon tempering. H. S. RAWDON AND SAMUEL EPSTEIN. *Bur. Standards, Sci. Papers* No. 452, 373-409(1922).—A study of the changes in structure resulting upon tempering was made in a series of 6 C steels ranging from 0.07 to 1.12% C, quenched from temps. varying from 750° to 1250° and tempered for different lengths of time at 100° to 650°. Upon quenching, martensite is formed throughout each austenite crystal in a manner strictly analogous to the freezing of solid-soln. alloys. A redistribution of C takes place and the conspicuous martensite plates are found to be distinctly lower in C than the "filling material" between the plates. The enrichment of the C in the "filling material" may be great enough in some steels as to allow small patches of austenite to persist after quenching. The changes in structure and in hardness which occur during tempering vary in character according to whether they take place above or below 250°. Below this temp., the structural changes are relatively slight and are best revealed in the higher C steels by an alk. oxidizing etching reagent or by immersion of a polished specimen in liquid air. At approx. 250° martensite and austenite, if present, undergo a transformation and the steel assumes a granular structural appearance and reacts vigorously toward dil. acid etching reagents. The granules, cementite particles, grow in size progressively as the tempering temp. above 250° is increased. Hardened steels, tempered by heating to temps. below 250°, show a slight decrease in hardness; above this temp., the decrease is rapid. Curves are given to illustrate the effect of the tempering period and temp. Steels containing austenite harden appreciably below 250° with the longer tempering periods, though no evidence was obtained to show that the steel regained or exceeded its initial hardness upon tempering as has been reported by other investigators.

V. O. HOMERBERG

The reduction and elimination of internal strains in steels by reheating followed by slow cooling. A. PORTEVIN. *Compt. rend.* 175, 959-61(1922).—The internal strains produced in 0.70 C steel bars on quenching may be removed by drawing in a salt bath for 1 hr. at 650°, and cooling slowly in ashes. A curve is given showing the removal of internal strain as a function of the drawing temps. from 0° to 650°. W. A. MURGER

Effect of temperature, deformation and rate of loading on the tensile properties of

low-carbon steel below the thermal critical range. H. J. FRENCH. *Bur. Standards, Tech. Papers No. 219*, 679-725(1922); cf. *C. A.* 16, 3461.—An app. for detg. tensile properties of metals at high temps. (including limit of proportionality) and the results of tests of several grades of boiler plate from 20° to 465° are described. The effects of cold and blue work on the properties of these steels throughout the range given are discussed, and in addn., some results are given showing the effect of tensional overstrain on the proportional limit at different temps. and its subsequent behavior with time. Effects of variations in rates of loading (both rapid and slow) and the modified app. used for this work are also described. V. O. HOMERBERG

Hardness and heat treatment of mining drill steel shanks. C. Y. CLAYTON. *Trans. Am. Inst. Mining Met. Eng.* 1208-M, 12 pp.(1923).—The hardness of mining drill shanks varies between 196 and 782 Brinell, the greater no. of steels showing values between 364 and 444. Methods of heat treating vary not only between different mines but also between blacksmiths at the same property. H_2O , oil and air are the quenching media used. The length of shank treated varies between $\frac{1}{2}$ and 8 in. The results of this brief investigation show that a standard method of heat treating must be adopted by each shop if drill shanks are to give satisfactory service. V. O. HOMERBERG

Review of present status of drill steel breakage and heat treatment. F. B. POLEY, C. Y. CLAYTON and H. S. BURNHOLZ. *Trans. Am. Inst. Mining Met. Eng.* 1206-M, 18 pp.(1923).—A general survey of 60 mines west of the Mississippi River suggests investigations which are proposed as desirable. V. O. HOMERBERG

Thermal treatment and overheating. J. HÉBERT. *Technique moderne* 14, 481-5, 600-7(1922).—H. shows how the Brinell test in conjunction with the Robert-Austens Roozeboom diagram can be used to det. the proper thermal treatment of steels, and describes in some detail the results of overheating and how to overcome them.

A. P.-C.

Effect of temperature on the mechanical and microscopic properties of steel. GEO. C. PRIESTER and O. E. HARDER. *Chem. Met. Eng.* 28, 111-15(1923).—Plain C steel contg. 0.16% C, when tested at temps. ranging from 20° to 600°, shows a max. in the max. stress, yield point and proportional limit curves at about 300°; however, these values do not exceed the corresponding values at 20°. It shows a min. in the reduction of area curve at approx. this same temp., with a less pronounced min. in the elongation curve. These changes in the phys. properties are due to the temp. at which the test is made and are not the result of the steel having been drawn or tempered at a certain temp. This is shown by the fact that when this steel is drawn, then cooled to ordinary temp. and tested, there is no max. or min. observed in the curves. Above about 300° the min. stress, yield point and proportional limit decrease almost as a straight line function of the temp. at which the test is made, and the effect on the max. stress is the most pronounced. There is a corresponding increase in the reduction of area and elongation, but the elongation is approx. constant above 400°. The impact toughness increases with the drawing temp. and appears to be nearly a straight line function of the drawing temp. The results of the impact tensile tests show a slight decrease in the tensile strength, reduction of area and elongation for specimens drawn at 100°. At higher drawing temps. these values increase with increase in the drawing temp. Microscopic examn. shows changes in the microstructure which correspond to the changes in the mech. properties at the higher temps. (400° to 600°), but do not seem to throw any light on max. and min. points in the curves for tests at 300°. V. O. H.

Effect of sulfur on rivet steel. G. K. BURGESS, et al. *Proc. Am. Soc. Testing Materials* 22, Pt I, 94-130(1922).—A preliminary report is given. The complete investigation will be published as a technologic paper of the Bur. of Standards.

V. O. HOMERBERG

Corrosion of iron. J. N. FRIEND. *Iron and Steel Inst. Carnegie Scholarship Mem.* 11, 156 pp. (1922).—A critical survey is given of the present knowledge of the corrosion of cast iron and steel. As a general rule, cast iron contg. large flakes of graphite is more susceptible to acid attacks than close-grained white iron. Ferrite is much more readily attacked by acids than the carbide. Alkalies have but slight effect upon cast iron. The corrosive action of water alone increases enormously with the temp. Artificially softened water is much more corrosive than untreated water. The introduction of alloying elements may affect the corrodibility of the metal indirectly (*e. g.*, Si tends to throw out graphite, render the metal more porous, and hence more susceptible to corrosion) or directly (S exists as sulfides, which markedly accelerate corrosion). The effect of C is directly dependent upon its condition. Graphite formation increases corrosion while with combined C the corrosion is much less. Mn tends slightly to reduce the corrodibility. P makes almost no difference in rate of corrosion. Si has no direct influence upon the rate of corrosion. Concerning the relative corrodibility of steel, wrought iron, and cast iron, no simple answer can be given. With neutral corroding mediums at rest, with few exceptions cast iron had the lowest rate of corrosion, with steel second, and wrought iron the most susceptible to attack. With neutral corroding media in motion, in general cast iron has the greatest rate of corrosion, with steel and wrought iron about equally corroded. Cast iron in general is very inferior to steel in its resistance to all concns. of acids. Contact between steel and cast iron increases markedly the rate of corrosion over all ranges of temp. Metals, such as Zn and those more readily oxidized than Fe, protect the latter. In paints to protect Fe against subaqueous corrosion by increasing the amt. of oil with const. wt. of pigment, there is a decided decrease in efficiency. With the same wt. of oil and an increasing wt. of pigment, the protection afforded increases to a point of max. efficiency and a further increase causes a distinct reduction in protection. The max. protection is offered by a paint 50% oil and 50% pigment. The chief functions of a pigment are to afford mechanical support to the linsoyn and to reduce the permeability of the paint. By increasing the relative amt. of pigment, greater protection should be afforded but there is a limit to the amount of pigment that a given wt. of oil can efficiently bind, and when once this limit is exceeded, the protective power is reduced. If linseed oil is heated in absence of air, the oil polymerizes, yielding a thicker litho oil which upon setting possesses the min. porosity and max. resistance to chem. disintegration. The iron when it leaves the mill is coated with scale or oxide which adheres very tenaciously. So long as this scale remains intact it affords a very efficient protection but if this oxide becomes cracked, corrosion proceeds with great rapidity. The cheapest method, and the one best calculated to prolong the economic life of the metal, is to paint the structure while their scale is still on, after first removing only the loosely adhering flakes and rust. The influence of strain upon the corrosion of Fe may be explained by studying the distribution of energy absorbed in rupturing a piece of Fe. As much as one half the work done in stretching the steel up to the limit of rupture may be stored up permanently. This energy is liberated when the metal is oxidized, the metal being attacked more readily, its potential rising with the increased strain. This reasoning fits into all the theories of corrosion (*cf.* C. A. 15, 3012). This explanation also fits the data obtained on stainless and high-Ni steels, which, while almost incorrodible in the normal condition, are relatively very much more corroded after having been strained. Corrosion reaches a max. at a temp. of around 80°. A curve, loss in wt. vs. temp., accurately shows the relative corrodibility at various temp.

E. F. PERKINS

Mechanism of the corrosion of iron and steel in natural waters and the calculation of specific rates of corrosion. R. E. WILSON. *Ind. Eng. Chem.* 15, 127-33 (1923).—Three reactions are involved: (1) the action of the H ion on the Fe to form ferrous

ions and a kind of at. H, neither gaseous nor yet ionic; (2) the formation of H_2O from the at. H with dissolved O; and (3) the formation of gaseous H from at. H.

V. O. HOMERBERG

A possible modification of the diagram iron-cementite. LOUIS GRENET. *Compt. rend.* 175, 1067-70(1922).—From a study of the magnetic properties of the allotropic forms of Fe in connection with their ability to dissolve C, G. suggests a modified diagram for the system Fe-C.

J. A. ALMQUIST

The crystallography of cementite. N. T. BELAIEV. *Rev. métal.* 19, 573-8(Abs.) (1922).—Two steels contg. resp. 1.8% C (=27% Fe_3C) and 0.60% C (=9% Fe_3C) were prepd. and examd. In the former, of the 27% of cementite, 11% is combined with ferrite to form pearlite, and the remaining 16% is free; while in the 2nd steel all of the cementite is combined to form pearlite. Conclusions: Cementite crystallizes (in steel) either as free (or proeutectoid) cementite, or with ferrite to form pearlite (pearlitic or eutectoid cementite); in the 1st case it is either prismatic or tabular, and in the 2nd it is tabular. The dimensions of the prisms of pro-eutectoid cementite in the pseudo-dendrites, or of the lamellae in the pearlite, are too small to be measured directly; but in each case the crystallographic angles are right angles. If the angle between the lamella of pearlitic cementite and the plane of the microsection is very small, the apparent width of the lamella on the section is very great, which usually permits of getting some idea of the cleavages of the cementite. They appear to belong to the regular or cubical system of crystn. Fe_3C is also found in meteorites, where it is called *cohenite*, the exterior form of which is also tabular. Direct measurements of large crystals of cohenite have shown that it belongs to the cubical system; whence it can be concluded that cementite also belongs to this system. The exterior form of cementite (prismatic or tabular) is due to the high linear velocity of crystn. Owing to the high ratio of surface to mass and to surface tension, cementite tends to contract to a globular or spheroidal form as soon as the temp. is raised sufficiently. This property was used unknowingly in the manuf. of the famous damascene steel. Five photomicrographs.

A. P.-C.

Investigation of duralumin. SHIBBI KONNO. *Sci. Repts. Tohoku Imp. Univ.* 11, 269-94(1922).—In quenching duralumin, the softer the quenching the more the immediate effect of hardening increases, and its aging effect, as well as its final hardness, decreases. In a quenching in oil at 100° or at higher temps., the aging effect vanishes. On the other hand, the harder the quenching the more the immediate effect decreases, and the aging effect and the final hardness increase, their max. values being obtained by quenching the alloy from 500° in H_2O . The above effect of quenching is due to the dissolution of Cu and Mg compds. in Al, the process of dissoln. or sepn. being very slow. Thus duralumin is in a somewhat hardened state, even if it is cooled very slowly from 500°; perfect annealing is obtained only by heating the alloy at 350° for 1 hr. or more. The quenching effects on the sp. elec. resistance of duralumin are very great and exactly similar to those on the hardness. Hence, the sp. resistance measurement is the most suitable method for the investigation of the hardening of duralumin. The alloys of Al-Cu show by quenching an immediate effect of hardening, but the effect of aging only very slightly. Hence, the immediate effect is partly due to the dissoln. of Al_2Cu in Al, but the principal cause of the aging effect of duralumin is not attributable to that compd. In the alloys of Al-Mg which contain about 1% of Mg, the immediate effect of quenching is always very small, but the aging effect is as great as that of duralumin. The aging effect, as well as the immediate effect of quenching the above alloys, is attributable to the dissoln. of Mg_2Si in Al, but not of metallic Mg; because, if Mg increases beyond 1%, the above 2 effects begin to diminish, and, with an increase of above 3% of Mg, almost vanish; but an addn. of both Mg and Si in the proportion of the compd. Mg_2Si

increases the same effects. A small quantity of Si is always present in Al as an impurity. The further addn. of about 4% of Cu and a small quantity of Mn (up to about 0.5%) to the alloys of Al-Mg increases the hardness, but not the aging effect. This alloy usually called duralumin has thus nearly the same aging effect as the alloys of Al-Mg. From the sp. resistance-temp. curves for quenched duralumin, it is concluded that a quenched alloy is tempered at 2 steps beginning at 210° and 280°, resp. The first step in the curves is due to the partial sepn. of Al_2Cu , and the second to that of Mg_2Si . The quenched duralumin expands at room temp., as the aging proceeds, as in quenched low-C steels. The above effect of quenching and the accompanying change in the phys. properties of duralumin are exactly similar to those in severely quenched C steels. The hardening of duralumin can be explained from Honda's theory of the hardening of steels.

V. O. HOMERBERG

Physical properties of the A.S.T.M. tentative standard white metal bearing alloys. J. R. FREEMAN, JR., *et al.* *Proc. Am. Soc. Testing Materials* 22, Pt. I, 207-11(1922).—In the Sn base alloys the difference in phys. properties is greater at normal temp. than at 100°. The Pb base alloys in general have lower compressive strength. The presence of Pb in an alloy causes a more rapid softening with increasing temp. The alloys made under com. conditions have in general at normal temps. a higher Brinell hardness than the alloys prepd. from pure metals under lab. conditions. A cylindrical test specimen 3 in. in length by 1 in. in diam. gives the same results as the $1\frac{1}{2}$ by $\frac{1}{2}$ in. specimen but the smaller specimen is easier to handle and gives more consistent results. The Brinell hardness tests using a 100-kg. load give results that are slightly but consistently higher than values obtained using a 500-kg. load. This indicates that all loads between 100 and 500 kg. should give results comparable with the 500-kg. load usually used.

V. O. HOMERBERG

Transformations in bronze, aluminium-bronze and brass. TSUTOMU MATSUDA. *Sci. Repts. Tohoku Imp. Univ.* 11, 223-68(1922).—As the result of thermal analysis, it was confirmed that the eutectoid transformation in bronze occurs at about 530° and 505° during heating and cooling, resp. The constancy of the transformation point, the relation between the thermal effect and the compn. of the alloy, and the change of the microstructure are all unmistakable evidence of a eutectoid transformation. Accompanying this transformation, discontinuous changes in phys. properties are noticeable. During heating, a discontinuous decrease in length and elec. resistance and also a discontinuous change in the direction of e.m.f.—temp. curve occur during the transformation. During cooling, the reverse change is observable. The equil. diagram of Cu-Sn alloys constructed from these results is given. The eutectoid transformation has also a considerable influence on the mech. properties. Those quenched from a temp. above the transformation point have a higher tensile strength and elongation, but a lower hardness, than those quenched from the temp. below it. If these changes are compared with those accompanying the A_1 transformation in steel, it is found that the changes in length and tensile strength occur in the same sense, but the changes in elec. resistance and hardness in the opposite sense. But the changes accompanying the transformation at 560° in Al-bronze are all in the same sense as those described above, while those at 460° in brass are different from the above. From the results of thermal analysis and microscopic examn., it is confirmed that the transformation at 560° in Al-bronze is a eutectoid change, as widely accepted. The temp. difference of the transformation points during heating and cooling amounts to 60° at the ordinary rate of heating and cooling. The physical properties of the alloys change discontinuously during the eutectoid transformation. A sudden change of length and elec. resistance are noticeable; thermoelectricity is also affected by this transformation. Mech. properties are also affected by the eutectoid transformation. The alloys quenched from the temps. above the transformation

point have the higher tensile strength and elongation and the lower hardness. The equil. diagram constructed from the results of the investigation agrees completely with that obtained by Curry. The complicated changes in the phys. properties may easily and satisfactorily be understood by assuming the eutectoid transformation to be a stepped change, as in the case of the A_1 transformation of steel. If the change in the various properties accompanying the eutectoid transformation is compared with that accompanying the transformation at 520° in bronze, a close agreement is found, but no such similarity will be found in the case of the transformation at 460° in brass. In the case of brass the transformation takes place chiefly in a range of temp. in the vicinity of 460° , and is found in the alloys contg. β . The corresponding abnormal change is found in the thermal analysis, thermal expansion, elec. resistance, thermo-electricity, and mech. properties. No corresponding change can be found in the microstructure. Hitherto the nature of the transformation in brass has been considered to be the eutectoid transformation as in the case of bronze and Al-bronze. But, from the present investigation, it was concluded that the transformation is a progressive one, having the same nature as the A_2 transformation in Fe. It is not a change of phase, but a change in at. energy, which is therefore only a function of temp. and independent of time. The temp. at which the transformation terminates during heating, or begins to take place during cooling, is termed the crit. point; it was found to be 480° . It is found that γ undergoes a transformation at 280° . Based upon the results of the investigation, a modified equil. diagram is presented.

V. O. HOMERBERG

Volatilization of zinc during the heating of brass in various mediums. LÉON GUILLET and MARCEL BALLAY. *Rev. métal.* 19, 748-58(1922).—Tests are described in detail. Loss of Zn in annealing brass depends largely on the nature of the medium in which the metal is heated. In oxidizing mediums the losses are much lower than those in reducing or neutral mediums, because of the formation of a film of ZnO which prevents volatilization of the Zn. Com. annealing is generally carried out at a relatively low temp. (600 – 700°), corresponding to a low vapor tension of the Zn, so that there is not a great loss of Zn; but annealing in an oxidizing atm. is preferable. During lab. tests considerable losses can occur; at about 800° losses are high, and heating at 600° for a few hrs. causes appreciable loss. In oxidizing atm. the losses are smaller but are already considerable at 800° . In order to eliminate practically all losses, when operating for a long time at high temps., annealing should be carried out in a sealed tube, e. g., of fused SiO_2 , the loss being then confined to the amt. of Zn required to spt. the free space in the tube. The vapor tension of Zn was detd. in solid brasses by comparing the vapor tension of the brass at temp. T to that of pure Zn at a lower temp. t . The method and app. used are described in detail. The vapor tension at 800° increases from 3 mm. for 38% Zn to 19 mm. for 43% Zn.

A. P.-C.

Recent progress in light alloys. LÉON GUILLET. *Rev. métal.* 19, 688-95(1922).—A brief review covering Al and Mg alloys. (Cf. C. A. 16, 701, 3298, 4177.) A. P.-C.

Some aluminium alloys. G. MASING. *Naturwissenschaften* 10, 1108-11(1922).—A summary of the 11th report to the Alloys Research Committee (cf. C. A. 16, 3462).

C. C. DAVIS

"Alpax," an aluminium alloy. DEFLEURY. *Technique moderne* 15, 31(1923).—A brief description of the properties of "Alpax," contg. 13% SiO_2 , patented by Pacz, which bears to ordinary cast Al the same relation as cast steel to cast iron. It is also known as "silumin."

A. P.-C.

Copper and copper alloys in the chemical and allied industries. WILKINSON STARK. *Chem. Age* (N. Y.) 30, 500-12, 555-8(1922).—S. discusses the resistivity of Cu and brass to the action of various corroding agents and their uses in the chem. and building industries.

V. O. HOMERBERG

Preparation and properties of pure iron alloys. I. Effects of carbon and manganese on the mechanical properties of pure iron. R. P. NEVILL and J. R. CAIN. Bur. Standards, *Sci. Papers* No. 453, 411-43 (1922); cf. *C. A.* 16, 4143.—Over 100 alloys with negligible amts. of impurities were prepd. from electrolytically purified Fe, C, and Mn of very high purity by fusion *in vacuo* in crucibles of magnesia prepd. especially to prevent contamination during melting. The compns. were so chosen as to bring out the effects on pure Fe of addns. of small amts. of C, addns. of small amts. of Mn, and of addns. of C and Mn together. The ranges in compn. of the alloys include from 0 to 1.6% C and 0 to 1.6% Mn. Ingots of 3 lbs. were made and rolled to $\frac{1}{2}$ in. plates from which specimens for testing were made. Ultimate strength, proportional limit, yield point, elongation, reduction of area, and Brinell hardness detns. were made and photomicrographs taken. In amts. below approx. 1% the ultimate strengths of the alloys were increased by C. The ratio of this strengthening effect to C content was not const., but was within the limits of 875 and 1,150 lbs. per sq. in. for each 0.01% C between the limits 0 and 0.70%. This strengthening effect was greater in the alloys of higher Mn contents. An approx. av. of the rate was 1000 lbs. per sq. in. for each 0.01% C. The hardness of the alloys was influenced by C in about the same manner as was the ultimate strength. The increase in hardness due to C was from 1.8 to 2.6 Brinell numbers for each 0.01% C, the rate being larger as the Mn contents increased. Reduction of area and elongation of pure Fe were 82.5 and 40.5%, resp. With the addn. of C these values were rapidly and regularly decreased with the increase in C until values little greater than 0 were reached around 1%. Increase in C beyond this point had little effect on ductility. These min. values were reached at lower C contents when the Mn was increased. C influenced the proportional limits of the alloys less than the other properties. Although the effects on proportional limits were less easily discernible, it could be seen that the max. values were reached at lower C contents than max. values for ultimate strengths and remained at its max. value over a wider range of C compn. Mn increased the ultimate strengths of the alloys only slightly, particularly with very small amts. of C present. Expressed quant., this rate of increase was about 90 to 250 lbs. per sq. in. for each 0.01% Mn. Mn influenced the proportional limits in about the same manner as it did the ultimate strengths. Brinell hardness numbers were increased about 0.5 by each 0.01% Mn when C was present. This rate was lower in the alloys of lower C contents. Mn had very little effect on the ductility of the alloys. The effects of Mn and C on the mech. properties of the alloys were each influenced by the other. The presence of C augmented the influence of Mn and *vice versa*.

V. O. HOMERBERG

Contraction and shrinkage of non-ferrous alloys as related to casting practice. R. J. ANDERSON. Bur. of Mines, *Repts. of Investigations* No. 2410, 13 pp. (1922); cf. *C. A.* 16, 4173.—The linear contraction of any alloy is a function of the exact chem. compn. of that alloy, and relatively small amts. of impurities affect the contraction. The wide range in contraction among the alloys of a given class, *e. g.*, brasses, bronzes, or Al alloys, indicates that it is poor practice to employ a rough figure as the contraction of alloys of a given class in general, since by so doing much difficulty arises in producing master patterns and in obtaining castings with a min. of wasters. Theoretically, the higher the pouring temp. the greater the contraction, as less metal can be held in a mold cavity at a higher temp. than at a lower temp. Actually, pouring at an intermediate temp. gives greater contraction than pouring at a high temp. or a low temp. on account of the effect of gas evolution in the case of alloys poured at high temps. The evolution of gas referred to causes actual expansion, thus interfering with the normal contraction and yielding less contraction. Other things being equal, the smaller the cross section the less the contraction for a given length. Other conditions being the

same, the greater the length for a given cross section the less the contraction. The linear contraction of alloys is a function of the kind of mold employed, the contraction being greater in chill molds than in sand molds, other conditions being the same. In sand molds, the contraction in a casting depends upon the contour of the pattern, the mass of the casting, and the size and distribution of the gates and risers—that is, the method of molding. Gas occlusion, owing to a high melting temp., causes less contraction owing to evolution of the gas when the metal freezes. The extent to which piping occurs on casting an alloy in an open-top ingot mold is a factor in detg. the suitability of an alloy for casting purposes, as this is an indication of the contraction in vol. In general, the less the depth of pipe the less the contraction in vol. A selected bibliography is included. Also in *Chem. Met. Eng.* **28**, 254(1923). V. O. HOMERBERG

Non-ferrous metals and alloys. WM. CAMPBELL, et al. *Proc. Am. Soc. Testing Materials* **22**, Pt. I, 200-6(1922).—Tentative specifications are given for brass pipe, standard sizes; for Cu pipe, standard sizes; and for seamless admiralty condenser tubes and ferrule stock. Tentative methods of chem. analysis are given for brass ingots and sand castings; and for bronze bearing metal. Tentative specifications are recommended for advancement to standard, namely, the tentative specification for Ni and for brass ingot metal, graded and ungraded, for sand castings. V. O. HOMERBERG

Thermal properties of aluminium-silicon alloys. J. D. EDWARDS. *Chem. Met. Eng.* **28**, 165-9(1923); cf. *C. A.* **16**, 4176.—An accurate detn. is made of the densities of Al alloys contg. variable amts. of Si. Data are given at temps. up to 1000°. Data are also given on crystn. shrinkage, total solid shrinkage and the tendency to form pipe. V. O. HOMERBERG

New applications of the expansion pyrometer in the thermal analysis of alloys. CHEVENARD. *Rev. universelle mines* **14**, 351-81(1922); *Rev. ind. minérale* No. **47**, 341-2(1922).—New modifications of the expansion pyrometer are described. Differential pyrometer. This is used in the thermal analysis of alloys by the method of Roberts-Austen. The curve previously drawn by the double galvanometer is obtained by a double-expansion pyrometer which moves an optical lever around 2 rectangular axes. It cannot be used like the galvanometer for fusion and solidification, but for thermal analysis it is simple, accurate and because of its optical system and its being unaffected by vibration, the curves are very precise. Galvanopyrometer. The relation of temp. and resistivity, the thermoelec. power and the magnetization of alloys can be measured. It consists essentially of a galvanometer with a movable frame combined with an expansion pyrometer. Changes in the surrounding temp. and vibration must be reduced as much as possible. The last is accomplished by a Julius absorber. Very precise curves are attainable. C. C. DAVIS

Nickel alloys retain their rigidity over an extended range of temperatures. P. CHEVENARD. *Compt. rend.* **175**, 486-9(1922).—A continuation of *C. A.* **16**, 1384. Alloys of (1) 15.0% Cr, (2) 22.6% Cr, (3) 9.0% Cr and 5.8% W, are compared with (4) pure Ni, (5) electrolytic Fe, and (6) 4.2% Ni—1.6% Cr—0.30% C steel, from 300-700° with a load of 10 kg./mm.² The order of values is 4, 3, 2, 6, 1, and 5. W. A. MUDGE

A study of the time factor in the etching of iron-carbon alloys. L. LOSKIEWICZ. *Rev. métal.* **19**, 681-7(1922).—Tests were carried out with 0.3, 0.6, 0.9, and 1.2% C steels, with various concns. of picric acid and of HNO₃ in water and in 95% alc. For higher dilns. than 5% HNO₃ or 1/4 satn. for picric acid, the time of etching increases very rapidly and the limits of the time required for proper etching are far apart. Elevation of temp. causes a regular decrease in the time required for etching (about 50% in passing from 15 to 25°). The time decreases as the C content increases, up to 0.9% C, and then remains practically const. Troostite, sorbite, pearlite and martensite are attacked in the order named, the first being etched most rapidly. In the presence of

troostite, martensite is very difficult to etch, probably owing to the formation of a local couple. Cementite was etched with basic reagents (picric acid, PbO, ferricyanide, each in the presence of NaOH) in a case-hardened steel (1.5% C at the surface) at about 100°. Dil. solns. require more time than stronger ones and give much lighter colors. The cementite of pearlite is practically unattacked even after 4 hrs. Illustrated with 15 photomicrographs and 4 sets of curves. A. P.-C.

The hardening of steels and metallic alloys. ALBERT PORTEVIN. *Rev. métal.* 19, 717-40 (1922).—A review. A. P.-C.

The cracking of cold drawn copper alloys. G. MASING. *Naturwissenschaften* 10, 1079-93 (1922).—A discussion with diagrams of the work of Heyn (cf. *Z. Metallographie* 1, 16 (1911); *Naturwissenschaften* 9, 321 (1921)); of Moore and Beckinsale (cf. *C. A.* 15, 1685; 16, 1734, 3294) and of Coker (cf. *Gen. Elec. Rev.* 1920, 1921). C. C. D.

Money: Properties and preparation of coinage alloys. HANRIOT. *Rev. sci.* 60, 760-8 (1922).—A general résumé of compn., manuf., and properties of Cu, Ag, and Ni alloys. W. A. MUDGE

The scientific principles in the manufacture of chilled rolls. EMIL SCHÜZ. *Stahl u. Eisen* 42, 1900-6 (1922).—Above a certain minimum, increased thickness of mold wall is without influence upon the depth of chill owing to the high heat cond. of the metal. Hot pouring is necessary to eliminate variations in shrinkage. The depth of chill should be at least 2.7% of the roll diam. Longer service will be obtained if the necks are softer than the roll itself. Hardness cannot be produced by C alone; Si is necessary. Too high C results in the sepn. of large graphite plates. Several analyses and photomicrographs of gray and white Fe rolls are given. W. A. MUDGE

Heating and cooling curves of large ingots. F. E. BASH. *Trans. Am. Inst. Mining Met. Eng.* 1201-S, 7 pp. (1923).—A test was made on an ingot 45 in. in diam. to det. the rate at which heat penetrated and the time necessary to bring the whole mass to a forging temp. Differences in temp. between portions of the interior as compared with the temp. of the furnace gases were detd. by inserting thermocouples in holes drilled parallel to the axis. After heating to a forging temp. the ingot was withdrawn from the furnace and the cooling curves were likewise detd. S. L. CHISHOLM

Sherardized coatings—where they serve best. F. L. WOLF. *Raw Material* 6, 12-14 (1923).—Results are given of a series of practical expts. made with a view to det. the amt. of coating deposited by sherardizing. V. O. HOMERBERG

Malleable castings. H. E. DILLER, et al. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 196-7 (1922).—A revision is proposed in the standard specifications for malleable castings. It is also recommended that the dimensions of the standard test specimen be modified. V. O. HOMERBERG

The thermal treatment of malleable castings. JEAN DURAND. *Compt. rend.* 175, 522-4 (1922); cf. *C. A.* 16, 3297.—Dilatation data for castings contg. a higher Si content (2.0%) confirm Charpy's results. At 725°, on cooling, the increase in vol. varies inversely with the speed of cooling owing to the transformation of Fe₃C to graphite. W. A. MUDGE

Specifications for steel castings for railroads. F. M. WARING, et al. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 81-93 (1922).—The S and P limits are set at 0.05 and the Mn at 0.85% as max. The physical properties are discussed. V. O. H.

Report of sub-committee III on inspection of the Fort Sheridan, Pittsburgh, and Annapolis tests. H. S. RAWDON, et al. *Proc. Am. Soc. Testing Materials* 22, Pt. I, 156-94 (1922).—Comparative results are given of corrosion tests on Cu-bearing and non-Cu-bearing materials. V. O. HOMERBERG

A new method of measuring corrosion in water. F. N. SPILLER AND V. V. KENDALL. *Ind. Eng. Chem.* 15, 134-9 (1923).—The corrosion of Fe pipe and the effect of velocity on corrosion are considered. V. O. HOMERBERG

Damage from oxygen in boiler feed water. G. H. GIBSON. *Elec. World* 81, 167 (1923).—The corroding of Fe in economizers and boilers is directly proportional to the concn. of the O in the feed water. Deaeration must be secured in some manner, such as by maintaining a partial vacuum if the water is not kept at its b. p. A. H. DICK

Failures in aluminium welding. LÉGRIS. *Rev. soudure autogène* 401-4 (Jan. 1922); *Rev. métal.* 19, 659-63 (Abs.) (1922).—The low resistance to corrosion offered by Al welds is attributed to the phys. condition of the metal of the weld, caused by fusion. An oxy-acetylene blowpipe was directed against a spot on an Al plate until incipient fusion without appreciable deformation. The spot behaved like a weld towards a corroding liquid. Similar results were obtained by substituting an elec. arc for the blowpipe. The quality of com. Al is measured by its purity ($= 100 - (\text{Fe} + \text{Si})$); but samples having apparently the same purity and mech. properties frequently have very different resistances to corrosion. The rapid corrosion of welds is most likely due to innumerable, microscopic blow-holes, which were present in the original ingots, and were completely flattened out in rolling; these recover their original shape as soon as the metal is heated to fusion. These blow-holes are not shown by the microscope; they are so small that they are completely filled up when polishing for examn. LeG., however, succeeded in showing their presence in a globule of molten and superheated Al; but in welds they are much smaller and more numerous, and are sepd. by thin walls which render the metal spongy and liable to corrosion over a large surface. Contrary to what happens with some other metals, the rapid corrosion is limited to the metal which has been actually molten during welding and does not extend to the neighborhood where the m. p. was not reached. Addn. of Cu to the metal used in making the weld decreases the corrodibility, 1% of Cu giving a weld with practically the same resistance as current grades of sheet Al. A sheet so welded was corroded to $1/3$ of its original thickness, and the weld behaved exactly like the sheet. Addn. of 1-1.5% Cu has practically no effect on the mech. properties of the Al; and test pieces so welded showed nothing abnormal after 6 months. When the welded pieces were subjected to alternate annealings and hammerings, the corrosion was quite uniform over the whole surface, including the weld line; the repeated hammerings decrease the porosity as does rolling. Such procedure is not commercially possible, and recourse should be had to the addn. of 1-1.5% Cu in the metal used for welding. Efforts should be made to turn out Al with a higher and more uniform resistance to corrosion, and if this is obtained by addition of, say, 1% Cu, the metal used for welding should contain about 2% Cu. A. P.-C.

Corrosion of lead-covered cables (BARTHOLOMEW) 4. Waterproofing composition [for metals] (U: S. pat. 1,441,605) 18.

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Mineral flotation. W. O. BORCHERT. U. S. 1,440,129, Dec. 26. Mech. features.

Oil-flotation apparatus for ore separation. D. STONEBRAKER. U. S. 1,442,306, Jan. 16. The app. comprises a series of flotation vats arranged in step-wise position so that liquid can flow from one tank to another. Froth-skimming devices are provided for the vats.

Apparatus for ore flotation by aeration and frothing. A. H. CONNORS. U. S. 1,441,560, Jan. 9.

Concentrating ores. A. C. VIVIAN. Brit. 186,760, Aug. 5, 1921. A flotation process for concg. ores and other heterogeneous materials contg. the more valuable metals as O-contg. compds., e. g., oxides or carbonates, consists in adding to the material org. compds., which are generally considered weakly acid, but are amphoteric or display acid-pseudo forms, contain N and O, and act upon the metals or metal compds. it is desired to sep., forming tarry or resinous complexes or decompn. products under the conditions which commonly occur in flotation processes with or without the use of known oiling or frothing agents. In some cases this action is assisted by the presence of an oxidizing agent, which may be the O of the air used for frothing. Examples of these org. compds., which may be added to or formed in the presence of the material to be sepd., are cupferron, oximes, isonitroso compds., amino acids, such as taurocholic acid, phenylglyoxime, dinitrosoresorcinol. The org. compds. may also be formed by the reaction between ketones or aldehydes and hydroxylamine, N_2O or NH_3 . Cf. *C. A.* **16**, 2103.

Crushing ores, etc. R. P. WHITELAW. Brit. 187,869, Nov. 24, 1921. In wet-crushing ores and other materials, the ore is disintegrated in predetd. defined stages and after each stage the material crushed to the required ultimate fineness is removed and the remaining unbroken or partly broken ore is presented for further disintegration. The ore may be subjected to a solvent liquid while being crushed, the crushed insol. portion of the ore being sepd. from the uncrushed material after each stage by agitating the liquid and then maintained in suspension in the liquid and floated off, the liquid being subjected to subsequent treatment for recovery of the sol. constituent of the ore. The process is applicable to the treatment of ore contg. gold. The removal of the finely crushed ore may be effected by directing on the material a fluid-pressure stream which reaches the interstices between the uncrushed rocks in the mass and removes the fine material. A suitable app. is specified.

Agglomerating ores. F. L. SMITH & Co. Brit. 187,220, Oct. 7, 1922. Fe ores or other powdered ores are agglomerated by being first heated in a rotary furnace under such conditions that they are slightly oxidized, and thereafter treated in a second app. such as endless band or a shaft, or the like, wherein they are subjected to the passage of air, or air and steam, so as to complete the oxidation and agglomeration.

Agglomerating ores. F. L. SMITH & Co. Brit. 187,601, Oct. 14, 1922. Powd. ores are heated in a rotary kiln to a temp. below that at which sintering occurs, and then subjected while at this temp. to pressure to produce a coherent porous mass. Air, or air and steam, may be blown through the heated ore, as described in 187,220 (above), before the pressure is applied.

Treating oxidized copper ores. H. L. SULMAN, T. J. TOPLIN, JR., W. G. PERKINS

and H. F. K. PICARD. U. S. 1,440,186, Dec. 26. Crushed ore contg. oxidized Cu compds. is heated with "town gas" or other reducing gas and, after reduction of the Cu, is leached with an ammoniacal solvent for Cu. Cf. C. A. 17, 53.

Treating lead carbonate ores with chloride solutions. N. C. CHRISTENSEN. U. S. 1,441,065, Jan. 2. A carbonate ore of Pb is treated with a warm concd. salt soln. contg. FeCl_3 and the resulting soln. contg. Pb chloride is sepd. and cooled to obtain a ppt. contg. about a third of the Pb of the original ore. The soln. is then electrolyzed with an Fe anode to ppt. the remainder of the Pb. The ppt. obtained by cooling is electrolyzed in molten condition with an inert anode to dissociate Pb and Cl and the Cl thus formed is used to reoxidize the FeCl_3 of the spent lixiviating soln. and form FeCl_2 for treating an additional quantity of ore.

Treating lead ores with chloride solutions. N. C. CHRISTENSEN. U. S. 1,441,061, Jan. 2. A soln. obtained by treating a Pb ore with chloride soln. to recover the Pb is heated by passing it through a horizontal tunnel where it is thrown into intimate contact with a current of hot gases by rapidly revolving cylinders which dip into the soln. This heating serves to evap. H_2O and may also acidify the soln. if hot roaster gases are used. PbCl_2 is smelted with C and CaO .

Treating sulfide ores of lead, copper and silver. N. C. CHRISTENSEN. U. S. 1,441,063, Jan. 2. Sulfide ores of Pb, Cu and Ag are treated with a hot concd. soln. contg. FeCl_3 to dissolve metals from the ore as chlorides and after sepn. of the soln. metallic values are pptd. from it.

Treating sulfide ores of lead and zinc. F. E. ELMORE. U. S. 1,441,072, Jan. 2. Pb-Zn sulfide ores or concentrates are treated with H_2SO_4 and the Pb compd. thus formed is dissolved by treating the mixt. with hot strong brine which leaves ZnS in the residue.

Extracting metals. AKT.-GES. B. FELDER-CLEMENT. Brit. 187,375, Aug. 13, 1921. In the reduction of W, Mo, Cr, Ti, etc., from their oxides by a thermo-aluminic process, the oxide and the Al are not mixed, but are placed in contact, the Al being either in powd. or compact form. The reaction may be carried out in a crucible; or, for making bars of W, Ti, etc., an Al tube filled with the oxide may be inserted in a refractory tube serving as a crucible. This may be subjected to a centrifugal action as described in 157,756.

Extracting and refining nickel. H. SEFTON-JONES. Brit. 187,111, Sept. 16, 1921. Ingots or other masses of pure Ni are made from impure Ni oxides by partially reducing the product with dil. HCl or a mixt. of HCl and HF , drying and consolidating the product by pressure, and finally subjecting the masses to calcination in the presence of reducing and desulfurizing agents such as charcoal and lime. In modifications, the preliminary reduction may be complete, or the impure oxide may be agglomerated before its reduction; the reduced product being crushed before the subsequent lixiviation.

Rotating horizontal kiln adapted for reducing ores. H. H. HINDSHAW. U. S. 1,441,351, Jan. 9.

Ore-roasting furnace. C. G. FINK. U. S. 1,440,533, Jan. 2. The furnace comprises superposed roasting hearths formed of an Fe alloy contg. 30-60% Cr, which has good heat cond.

Water-cooled fittings for metallurgical furnaces. F. SCHIEGRIS and M. PASCHKE. U. S. 1,441,178, Jan. 2. Fittings such as tuyers which are provided with H_2O -circulating passages for cooling them are formed of Al or an Al alloy.

Premelting scrap for open-hearth furnaces. C. B. JOHNSON. U. S. 1,439,901, Dec. 26. In the manuf. of steel in an open-hearth furnace, scrap is melted, before charging it into the open-hearth furnace, by dumping it into a bath of previously melted metal and blowing air through the molten bath to raise its temp.

Apparatus for scouring ores or ore pulps. E. W. MYERS. U. S. 1,441,165, Jan. 2.

The app. comprises a series of constricted conical passages within which nozzles are placed which supply steam under pressure.

Blast furnace for smelting ores. U. A. GARRRD. U. S. 1,439,957, Dec. 26.

Casting metals. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON. Brit. 187,943, July 5, 1922. Molds for casting oxidizable metals such as Mg are coated with materials adapted to give off in contact with the molten metal gases or vapors which are inert or easily oxidizable and the oxidation products of which do not act upon the metal. The material may be dusted or sprayed on the mold surface or may be applied by melting or in soln. Mg oxalate and S are mentioned as examples.

Furnace for melting metals in crucibles. H. G. WELLMAN and C. D. GILPIN. U. S. 1,440,515, Jan. 2. The furnace is arranged for heating both by elec. current and by gas or oil.

Apparatus for sintering flue dust. L. C. EDGAR. U. S. 1,442,023, Jan. 9. A pipe extends from a sintering pan to an exhaust fan via a cooling and cleaning device for treating the products of combustion passing to the fan.

Furnace adapted for "differential" heat treatment of projectiles. F. C. LANGENBERG and J. F. FETTERLY. U. S. 1,440,546, Jan. 2.

Heat-treating projectiles or similar metal articles by whirling combustion gases. W. J. HARRIS, JR. U. S. 1,440,540, Jan. 2.

Casting rods of metals of high melting point. H. T. REEVE. U. S. 1,442,444, Jan. 16. Metals or alloys of high m. p. such as those having a m. p. above 1000° are obtained in the form of small rods by forcing the molten material into a tube of fused SiO_2 or other refractory material and allowing it to solidify in the tube before removal.

Iron and steel. A. NAITO. Brit. 187,810, Sept. 29, 1921. Magnetic sand or finely divided Fe ore is mixed with powd. coal and coked and the product heaped up in the open air, the Fe being converted into sol. form by passing through the mass SO_2 or Cl gas or by pouring sea water or a soln. of caustic alkali over the heaps. The heaps are then left exposed to the air until a proportion of the sol. salts is converted into insol. salts, and the product is obtained in the form of hard lumps or masses which are smelted with a suitable flux in a furnace to produce pig iron.

Unstainable steel. I. ATTCHISON. Brit. 187,310, July 14, 1921. Unstainable articles are formed from ferrous material contg. Cr or Ni or both, by casting, rolling, or forging from material having the metallic compn. of unstainable metal but contg. a higher proportion of C than is permissible in the finished article and then decarburizing the whole or part of the surface layer so as to obtain an unstainable surface where required. E. g., a ferrous casting contg. Cr 12% and C 1.5%, after cleaning by sand-blasting or pickling and machining to final dimensions, is heated to a temp. of 1200° for a period of 10 hr. in a container through which a stream of H is passed and allowed to cool therein. Solid decarburizing reagents such as mill-scale or hematite iron ore may, however, be used. If, after casting, the articles are too hard for machining, they may be softened by heating to a temp. of 750° and cooling in air.

Manganese steel. J. M. BLAKE. U. S. 1,439,939, Dec. 26. A steel contg. Mn 4.25, C 0.42 and Si 0.25% is used for making cast annealed roll tires or other articles.

Briquetting cast iron particles. W. C. MAIN. U. S. 1,439,907, Dec. 26. Briquets adapted for furnace charging are formed of cast Fe particles and the superficial portion of the briquet is rendered highly cohesive by treatment with dil. HCl soln.

Rustproofing iron or steel. A. MAI. U. S. 1,440,092, Dec. 26. Fe or steel articles are rustproofed by immersing them in a soln. which may be formed from NaOH, KNO_3 , $\text{Ca}(\text{OH})_2$ and H_2O at $120\text{--}130^{\circ}$ and causing production of KOH in the soln. in contact with the metal.

Cleaning and surfacing sheet steel. S. M. NOYES and S. PRACOCK. U. S.

1,440,619, Jan. 2. Sheet steel contg. cementite and ferrite in its surface is ground or buffed to remove the cementite and leave channels in the ferrite and the ferrite is then spread over the surface by a polishing operation so that it fills the channels and inhibits subsequent oxidation of the surface.

Alloys. BRITISH THOMSON-HOUSTON CO., LTD. Brit. 187,089, Aug. 29, 1921. An alloy suitable for engine cylinders, piston rings, and molds for rubber articles such as tires, consists of at least 50% of Al, at least 2.5% of Si, and the remainder Cu. The alloys may be made by melting the elements together, or from Al and Cu silicide, or from Al silicide and Cu silicide.

Alloys. F. GREINER. Brit. 188,049, July 28, 1921. Fe alloys contg. Si are made by melting together briquets or masses of ferro-Si prep'd. by the process described in 146,230 (C. A. 14, 3400) with the other ingredients of the alloy, such as pig iron, scrap iron, or steel.

Iron alloys. F. GREINER. Brit. 187,729, July 28, 1921. The process described in 146,230 (C. A. 14, 3400) is now applied to the production of Fe alloys contg. in addn. to Fe, with or without one or more of the elements Si, Mn, P, W, Ni, Co, etc., another element such as B, or to the introduction of a reagent such as an alkali or a thermoluminescent mixt. The materials may be enclosed in shells made of sheet metal, wood, or varnish, and in cases in which it is necessary to disintegrate the ingredients this is preferably done by granulation, and not by grinding or crushing. Granulated cast Fe may be mixed with cement and made up into briquets, each of which contains a package of Na_2CO_3 .

Iron alloys. J. C. GILLOTT. Brit. 186,982, July 6, 1921. Workable low-C iron alloys contg. Cr in smaller proportion than Fe are made by blowing in a converter molten metal contg. C, intentional overblowing being avoided. The charge to be blown may consist of ferro-Cr dild. with pig-iron, scrap steel, or other form of Fe; or high-C Fe may be mixed with low-C ferro-Cr or high-C ferro-Cr may be mixed with low-C iron; or both materials may contain C. Si is preferably present in or added to the charge in sufficient proportion to raise the temp. by oxidation during the blowing. The finished alloy is deoxidized by means of Mn or other deoxidizer.

Magnetic alloy sheets. A. E. WHITE. Brit. 181,401, Dec. 8, 1920. Means are provided for exerting a definite unvarying pressure during the final pass. The rolling-mill may comprise a lower roll supported by hydraulic cylinders supplied from an accumulator loaded by wts. The complete process preferably also comprises casting exceptionally pure ingots, heating the ingots slowly to approx. 1200°F . before bringing them to rolling temp., producing a pack, the necessary heating between passes being conducted in a muffle furnace, the sheets being out of contact with the heating flame and surrounded by a suitable atm., heating the sheets prior to the final pass to such a temp. that they are discharged at or about the temp. of recalcence, and annealing.

Copper-nickel-lead-tin alloy. J. C. STONE. U. S. 1,442,742, Jan. 16. An alloy which is adapted for acid-resisting pipe fittings is formed of Cu 70-76, Ni 17-20, Pb 1.5-6 and Sn 2.5-5%.

Nickel-copper-aluminium alloy. L. CAMMEN. U. S. 1,439,865, Dec. 26. An alloy which is hard, tough and resists corrosion is formed of Ni 60-70, Al 10-3%, and Cu.

"Alloying alloys" from chromium ores. W. BENNETT. U. S. 1,441,479, Jan. 9. A Cr ore is reduced with coke, lime and fluorspar by the action of an elec. arc, the resulting slag is removed and the remaining material is treated with a decarbonizing material rich in Si, e. g., a mixt. of mill scale, chromite ore and Si; and slag is again sepd. The alloy produced may be combined with Ni, Co, Mo or V to modify its properties.

Rust remover. G. L. WILLIAMS. U. S. 1,439,780, Dec. 26. A compn. adapted for removing rust from ferrous metals is formed of an acid mixt. contg. gelatinized starch and ZnSO_4 or a similarly acting salt.

Arc welding and metal-cutting electrodes. W. H. BOORNE. Brit. 185,580, July 19, 1921. An electrode for arc welding and metal-cutting comprises a metal rod wound with a carbonaceous fiber and covered by an extrusion machine with a coating of magnesite, Al, and Na silicate, the fiber being satd. with a satd. soln. of Na baborate, and the winding and covering with the mixt. being effected while the fiber is wet with the soln. The winding may be effected transversely and the coating mixt. may include crocidolite asbestos or amosite (blue amphibole asbestos contg. about 1% of SiO_2 and 38.5% of FeO), graphite contg. not less than 98% C, and granulated Mg. The coating materials are intimately mixed and ground to a fine powder which is mixed to a stiff paste with a soln. of Na silicate of strength 40°Tw . Cf. 132,354, 152,257, and 157,509 and 166,479.

Electrodes for metal arc soldering. E. H. JONES. U. S. 1,441,685, Jan. 9. Electrodes of metal are coated with a cement which sets on drying, e. g., a mixt. of slag sand, lime and H_2O . U. S. 1,441,686 specifies coating of mild steel or other base metal electrodes with Ni, Cr and asbestos yarn. U. S. 1,441,687 relates to electrodes formed of mild steel, superficially carbonized by case-hardening and coated with asbestos yarn or other "second class" conductor. U. S. 1,441,688 specifies electrodes for welding formed of rods of mild steel surrounded by cast Fe (to secure the proper proportion of C and Fe).

Ingot-mold. E. GATHMANN. U. S. 1,440,535, Jan. 2.

10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER

Organic chemistry nomenclature of China. REPORT OF GENERAL COMMITTEE ON SCIENTIFIC TERMINOLOGY OF CHINA. *Science (China)* 7, 489-503(1922).—The system adopted follows essentially the principles of the Geneva nomenclature, with the avoidance as far as possible of both the invention of new characters and the transliteration of western sounds.

WM. H. ADOLPH

Natural rotatory dispersion and its application to chemical analysis and research. E. DARMOIS. *Rev. gén. sci.* 33, 670-7, 710-6(1922).—Mathematical and phys. treatment of the theory and technic of the detn. of rotatory power and rotatory dispersion, with examples of applications to chem. problems. The detn. of the dispersion ratio (α_M/α_N) in addn. to the rotatory power (α_D) is advocated for the study of the active mol. The dispersion ratio is characteristic of the chem. nature of the compd., being const. for the two antipodes and all mixts. of the two. With compds. having normal dispersion this ratio is practically const. for homologous series, independent of the solvent (neutral), concn., and temp. (20-100°). Substitutions have the max. effect when near the asym. C. A marked effect is noted for double bonds. Compds. having abnormal dispersion are less productive of generalizations. A. C. PURDY

The nature of the multiple carbon bond. H. J. PRINZ. *Ber.* 55B, 3437-9(1922).—A brief resumé of previously developed ideas of P. The increased energy of the C atoms of unsatd. compds. detrs. their activity, while the energy necessary to break the bond detrs. the strength of the bond. I. P. ROLF

Purification of methanol by means of sodium hypochlorite. R. C. MENZIES. *J. Chem. Soc.* 121, 2787-93(1922).—AcMe is attacked instantly by NaOCl in the cold but MeOH is only slowly attacked unless the temp. is raised above 50°. EtOH and fermentation BuOH are also attacked vigorously by NaOCl at higher temps. Curves are given showing the behavior of MeOH free of and contg. AcMe with NaOCl. De-

tails of an expt. are given in which 1 l. MeOH contg. 120.8 g. AcMe mixed with 1 l. H₂O was treated with 2800 cc. NaOCl soln. (144.7 g. available Cl per l.) and from which 74.7% of the MeOH was recovered, with an AcMe content of 0.077%. In this mixt., contg. 4.03% AcMe, the temp. rise after addn. of the NaOCl in 3 portions was 52.5°. The AcMe content of wood spirit treated on a large scale ought not to exceed 2.5–3%. This method of purification is of advantage since the NaOCl does not attack Fe.

C. J. WEST

Equilibrium in systems composed of water and alcohols: methanol, pinacol, glycerol and erythritol. N. A. PUSHIN AND A. A. GLAGOLEVA. *J. Chem. Soc.* 121, 2813–22 (1922); cf. *C. A.* 9, 1417.—Pure MeOH crysts. at –96°. Its cooling curve is that characteristic of a pure substance. The equil. diagram of the system MeOH–H₂O is characterized by 2 branches, which cross at the eutectic point (–100.5°). It follows, therefore, that in the cryst. state MeOH does not form any definite compds. with H₂O. Their existence in the liquid state at the ordinary temp. is still less probable. With a pinacol (A) m. 41.1°, the equil. diagram is found to consist of 5 branches: From pure A to a mixt. contg. 80 mol. % of A, corresponding to a eutectic point at 29.4°; from 80 to 50 mol. % A, the max. of the curve corresponding to the compd. C₂H₅(OH)₂·H₂O, crystg. at 41.25°; from 50 to 38.5 mol. % A, corresponding to a 2nd eutectic point at 40.4°; from 38.5 to 14.3 mol. % A, the max. corresponding to the hexahydrate, crystg. at 45.4°; from 14.3 mol. % A to pure H₂O. Glycerol, m. 18°, and H₂O form an eutectic at 28° and an average concn. of C₃H₅(OH)₂ of 20 mol. %. The f. p. const. for C₃H₅(OH)₂ was found to be nearly 3.1. The detn. of the f. p. of C₃H₅(OH)₂ affords a sensitive and precise method for the quant. detn. of even small quantities of H₂O. The eutectic point for erythritol (B)–H₂O lies at –4.4° with a concn. of 3 mol. % of B. B forms with H₂O neither compds. nor solid solns. and in the cryst. state B and ice yield mechanical mixts. only.

C. J. WEST

Reduction of nitriles with hydrogen in the presence of nickel. HANS RUPE AND KARL GLENZ. *Helvetica Chim. Acta* 5, 937–42 (1922).—The reduction of C₆H₅CN with Na and EtOH gave C₆H₅NH₂, but the use of H in the presence of Ni gave dihexylamine, b₁₂ 109–15°; hydrochloride, glistening leaflets. In the same way PhCH₂CN gave diphenylethylamine, the hydrochloride of which forms glistening leaflets. Nitroso derivative, leaflets, m. 53–4°. PhCH₂CH₂CN (b₁₂ 128–30°) gave diphenylpropylamine, analyzed as the hydrochloride, glistening leaflets; nitroso derivative, felt-like needles, m. 55–6°.

C. J. WEST

Organic arsenic compounds. VIII. Action of cyanogen bromide on tertiary arsines. WILHELM STREINKOFF, HANS DONAT AND PAUL JAEGER. *Ber.* 55B, 2597–614 (1922); cf. *C. A.* 16, 1740.—The work on the action of BrCN on tertiary arsines has been extended to other arsines, including (O₂NC₆H₅)₃As (A). Working with A was rendered difficult on account of its slight soly. so that the expt. had to be carried out in fused BrCN at about 50° instead of in cold Et₂O or petr. ether. Under these conditions A does not add BrCN and as Ph₃AsBrCN is still quite stable at this temp. this result shows that by greatly increasing the negative character of a tertiary arsine its power to add the negative constituents of BrCN may be completely destroyed. The other arsines studied were prepd. from primary or secondary haloarsines with alkylmagnesium bromides; the prepn. of AsMeEtPh and AsMePrPh offered no difficulties but in making AsMePhCH₂Ph from MePhAsCl and PhCH₂MgCl considerable (PhCH₂)₂ was sometimes formed also. AsEtPr₂, AsEt₂Bus, AsEtPh₂ and cyclopentamethyleneethylarsine (B) gave with BrCN under the conditions described in earlier papers solid cryst. bromocyanides, those of AsEtPr₂ and B being so hygroscopic that their m. ps. could be detd. only with special precautions. Even in the cases where bromocyanides could not be isolated in solid form, however, their existence could be shown by their

hydrolysis to the hydroxybromides. The decompn. of these bromocyanides proceeds cleanly and in only one direction only in the cases of those of AsEtPh_2 , $\text{AsEt}(\text{CH}_2\text{CHMe}_2)_2$, AsMeEtPh and AsMePrPh , with the formation of EtBr by the first two and MeBr by the last two, together with Ph_2AsCN , $(\text{iso-Bu})_2\text{AsCN}$, EtPhAsCN and PrPhAsCN , resp. While, however, Et is cleanly split off before Pr in the N series, EtPrAsBrCN gives a mixt. of EtBr , PrBr , Pr_2AsCN and EtPrAsCN . The decompn. of B . BrCN is quite complicated and could not be completely elucidated owing to the small amt. of material available; it was established, however, that there are formed EtBr , BrCN and a mixt. which on heating with MCl at 100° gives small amts. of a periodide (C) and *cyclopentamethylenemethylethylarsonium iodide* (D), the formation of C indicating the presence of a cacodyl halide or cyanide (in this case probably $(\text{CH}_2)_4\text{-AsCN}$) and that of D showing that B was present. The decompn. therefore proceeds in at least 2 directions: (1) into the original components, like Ph_2AsBrCN , and (2) into EtBr and $(\text{CH}_2)_4\text{AsCN}$, like the bromocyanides of aliphatic and aliphatic-aromatic substituted tertiary arsines; there were no indications of the rupturing of the As-contg. ring . The facts thus far obtained may be summarized as follows: Tertiary arsines, unlike tertiary amines, react, even when 2 or 3 Ph groups are present, with BrCN to form very easily hydrolyzed but otherwise relatively stable bromocyanides which, again unlike the amines, decomp. only at high temps. Ph_2AsBrCN decomp. largely into the original components; all bromocyanides of aliphatic and aliphatic-aromatic substituted arsines yield alkyl bromides and cacodyl cyanides, Me splitting off before Et , Pr and Ph , Et before iso-Bu and Ph , Et and Pr with about equal ease. The firmness of the attachment of the hydrocarbon residues to As and also, according to the work of v. Braun, to N is different from that of their attachment to C , at least in the unsym. pinacols (cf. Meerwein, *C. A.* 14, 1309). The $(\text{CH}_2)_4\text{As}$ ring is more stable than the piperidine ring towards BrCN . The greater stability of arsine bromocyanides as compared with those of the amines is due to the more metallic and therefore more positive character of the As , as shown by the fact that the introduction of strongly negative groups (as in A) destroys the power of arsines to form bromocyanides. *Ethylidiphenylarsine* (25.6 g. from 33 g. Ph_2AsCl and EtMgBr), b_{10} $162-3^\circ$; bromocyanide, m. 75° . *Diphenylcyanoarsine*, b_{28} $207-9^\circ$, m. 31.5° . *Ethylidiphenylarsine hydroxybromide*, m. 97.5° ; *hydroxy-pyricate*, lemon-yellow leaflets from dil. alc., m. 116° . *Ethylidipropylarsine* (yield, 46%), strongly refractive, b_{14} $60-4^\circ$; bromocyanide, is so sensitive to moisture that it deliquesces when introduced into a m. p. tube and evolves a HCN -like odor; *hydroxybromide*, is extraordinarily hygroscopic; *hydroxy-pyricate*, vivid yellow cryst. powder from dil. alc., m. 85.5° . *Ethyl-diisobutylarsine* (yield, 52.5%), strongly refractive, b_{18} 86° ; bromocyanide m. 69° ; *hydroxybromide*, is of a salve-like consistency; *hydroxy-pyricate*, fine yellow needles from dil. alc., m. 82° . *Diisobutylcyanoarsine*, b_{18} 116° . *Methylethylphenylarsine* (yield, 57%), b_{11} $93-9^\circ$; bromocyanide, oil; *hydroxybromide*, m. 83° . *Ethylphenylcyanoarsine*, b_{28} $148-50^\circ$. *Methylpropylphenylarsine* (yield, 66%), b_{11} $105-6^\circ$; *hydroxybromide*, m. 146° ; *hydroxy-pyricate*, vivid yellow needles from H_2O , m. 84° . *Propylphenylcyanoarsine*, b_{30} $150-5^\circ$. *Methylphenylbenzylarsine* (11.4 g. from 30 g. PhCH_2Br as the Grignard reagent and 35 g. MePhAsCl), b_{17} $174-7^\circ$; *hydroxybromide*, microcryst. powder from $\text{EtOH-Et}_2\text{O}$, m. 147° ; *hydroxy-pyricate*, yellow needles, m. 119° . B (yield, 12% from 2 mols. EtAsCl_2 and 1 mol. $(\text{CH}_2)_4(\text{MgBr})_2$), $b_{12.5}$ $62-4^\circ$, has a not unpleasant, more ethereal than arsine-like odor when fresh but develops the typical arsine odor in a day. D , obtained smoothly from B and an excess of cold MeI , m. 276° . *Cyclopentamethylenediethylarsonium iodide* is similarly obtained with EtI . The bromocyanide of B is too sensitive to moisture for a m. p. detn.; *hydroxybromide*, m. 71° . C. A. R.

Investigations in the field of the olefin-magnesium compounds. I, II, III. W. KRESTINSKY. *Ber.* 55B, 2754-62, 2762-70, 2770-4(1922).—In syntheses with the aid

of Mg org. compds., halogenated olefins of the type $\text{CH}_2\text{:CHBr}$, in which the same C atom bears the halogen and the double bond, have thus far hardly been used at all, probably because of the general belief that such halides do not react at all or do not react normally with Mg. The object of the present work was to fill in the gap existing between the Mg compds. of satd. alkyl halides and those of C_2H_3 derivs. *Action of Mg on isocrotyl bromide.* $\text{Me}_2\text{C:CHBr}$ (A) dild. with Et_2O does not react with Mg under the usual conditions and only sluggishly and incompletely on warming or addn. of I, but if the Mg is first activated with I according to Baeyer, then covered, still warm, with dry Et_2O and treated with the A in Et_2O , the reaction begins generally spontaneously, otherwise on gentle heating, and then proceeds so vigorously that occasional cooling becomes necessary. It is best, as soon as the reaction begins, to immerse the flask in a bath at $18-20^\circ$, for if the temp. rises markedly there begins an intense evolution of gas and the Mg org. complex apparently decomp. in part; on the other hand, if the temp. is kept too low, the reaction may stop. The app. should be provided with an efficient stirrer and a Hg seal and the A added slowly to avoid local superheating. A considerable portion of the Mg does not react; at the end of the reaction the contents of the flask consisted of a dark soln. which on warming began to evolve gas again. As the end point of the reaction was taken the moment when the reaction mixt., without being warmed, stopped boiling of itself. The evolved gas absorbed Br eagerly and decolorized KMnO_4 but did not react with Béhal's reagent or $\text{NH}_2\text{-CuCl}$ and gave no ppt. with HgCl_2 ; its bromide chiefly b_1 , $54-6^\circ$, b , $149-51^\circ$, d_4^{20} 1.7827, n_D^{20} 1.51406, 1.51186 at 15° and 20° , and is apparently α,β -dibromoisobutane; the higher boiling fraction, b_1 , $107-9^\circ$, seems to be a tribromoisobutane; there were no indications of the presence of tetrabromides $\text{C}_4\text{H}_6\text{Br}_4$. The gas must therefore be $\text{Me}_2\text{C:CH}_2$ (B), formed according to the scheme: $\text{Me}_2\text{C:CHMgBr} \rightarrow \text{Me}_2\text{C:C} = \text{or } -\text{CH}_2\text{CMe:CH-} + \text{HMgBr}$ (1); $\text{Me}_2\text{C:CHBr} + \text{HMgBr} = \text{Me}_2\text{C:CH}_2 + \text{MgBr}_2$ (2). To det. the fate of the bivalent radical formed according to (1) 213 g. A was treated with 29 g. Mg and 5 g. I; this gave 251. B, 30 g. unchanged A, about 15 g. of a product (C) b. $131-4^\circ$, free from halogen but contg. 10.45% O, and a fraction whose b. p. rose continuously. By means of a freezing mixt. C was sepd. into a substance f. -23° and m. -12° and another which froze only in solid CO_2 . The former still contained O (8.62%), reduced $\text{NH}_3\text{-Ag}_2\text{O}$ with mirror formation, colored fuchs. SO_4 , apparently did not react with $\text{H}_2\text{NCONHNH}_2$, decolorized Br with explosive violence, reacted with EtMgI with distinct evolution of heat. The radical $\text{Me}_2\text{C:C} =$, therefore, must have reacted in some way with the Et_2O , possibly with formation of an addn. compd. of the oxonium type. *Action of AcH on $\text{Me}_2\text{C:CHMgBr}$; synthesis of methylisocrotylcarbinol (D).* From 195 g. A, 37 g. Mg and 100 g. AcH were obtained 0.8 l. B and, after decomp. with H_2O and refluxing about 7 hrs. with aq. KOH to remove any unchanged AcH, 71 g. of a crude product yielding 12 g. EtOH , 20 g. D, 9 g. of a fraction (E) b. $185-205^\circ$, and 4 g. of a fraction b. $228-32^\circ$. D has a pleasant alc. odor, decolorizes Br and KMnO_4 , d_4^{20} 0.8384, n_D^{20} 1.43159, 1.43430, 1.44098, 1.44721 for C, D, F and G at 20° ; 4 g. heated 20 hrs. at 100° in a sealed tube with Ac_2O gives 3 g. of a mixt. of a hydrocarbon, apparently α,α -dimethylerythrene (δ -methyl- α,γ -pentadiene), b. $75.5-6.0^\circ$, d_4^{20} 0.72155, n_D^{20} 1.44664, and of the acetate of D, b. $140-6^\circ$. E on fractionation under 15 mm. is sepd. into 2 substances, apparently isomeric alcohols $\text{C}_7\text{H}_{14}\text{O}$; one b_1 , $80-7^\circ$, d_4^{20} 0.8596, n_D^{20} 1.55344, and the other b_1 , $87-97^\circ$, d_4^{20} 0.8763, n_D^{20} 1.45854. *Synthesis and transformations of isopropylisocrotylcarbinol (F).* From 165 g. A, 29 g. Mg and 88 g. Me_2CHCHO were obtained 8 g. iso-BuOH, 22 g. F and 13 g. of higher boiling fractions ($175-220^\circ$). F b. $161-3^\circ$, d_4^{20} 0.8444, n_D^{20} 1.44493, has a peculiar pleasant odor, decolorizes Br; 7.5 g. heated 30 hrs. at 100° with Ac_2O gives 1.5 g. of the acetate, b. $177-80^\circ$, d_4^{20} 0.8270, n_D^{20} 1.43288, and 2 g. β,ϵ -dimethyl- α,γ -hexadiene (β -methyl- δ -isopropylerythrene) (G), b. $116-8^\circ$, d_4^{20} 0.7412, n_D^{20} 1.45024, does not solidify -80° ,

gives with KMnO_4 a little Me_2CO , a small amt. of a cryst. erythritol, HCO_2H , AcOH and $\text{Me}_3\text{CHCO}_2\text{H}$. **F** with KMnO_4 yields Me_2CO , two substances $\text{C}_4\text{H}_{10}\text{O}_4$ (apparently stereoisomeric α, α -dimethyl- α' -isopropylglycerols; one, difficultly sol. in Et_2O , m. 159–60; the other, easily sol. in Et_2O , very hygroscopic, m. 73–5°), HCO_2H , AcOH , $\text{Me}_3\text{CHCO}_2\text{H}$ and a non-volatile acid forming a cryst. semicarbazone and a calcium salt, the compn. of which, $(\text{C}_4\text{H}_7\text{O}_4)_2\text{Ca} \cdot \text{H}_2\text{O}$, indicates that the acid is dimethylpyruvic or isobutyrylformic acid. The formation of **G** from **F** is most plausibly explained by assuming that the Ac_2O not only acetylates the HO group of the **F** but that 1 mol. AcOH simultaneously adds at the double bond and then splits off in a different way. As a matter of fact, when larger amts. of **F** (25 g.) are treated with Ac_2O , there are obtained, besides 7 g. **G** and a small amt. of a substance b. 224–7°, two isomeric acetates of **F**: 2 g. b. 167–70°, d_4^{20} 0.88676, n_D^{20} 1.43739, and 5 g. b. 174–6°, d_4^{20} 0.88226, n_D^{20} 1.43238. Sapon. of the first with $\text{Ba}(\text{OH})_2$ gives an alcohol b. 158–61°, d_4^{20} 0.8449, n_D^{20} 1.43679, and the second yielded an alcohol b. 160–5°, d_4^{20} 0.8455, n_D^{20} 1.43789. Dehydration of **F** with Al_2O_3 . Passed over Al_2O_3 at incipient redness, **F** gives chiefly diisocrotyl, $\text{Me}_3\text{C}:\text{CHCHC}:\text{CMe}_2$, b. 132–8°, solidifies in ice-salt (dibromide, m. 65°), and a compd., probably α, α -dimethyl- γ -isopropylallene (β, ϵ -dimethyl- β, γ -hexadiene), b. 119–23°, solidifies at –80° but not at –23°, d_4^{20} 0.7637, n_D^{20} 1.45054. Synthesis of phenylisocrotylcarbinol (**H**). **H**, from **A**, **Mg** and **BzH**, liquid of a strong, peculiar odor, b. 122–5°, d_4^{20} 0.9861, n_D^{20} 1.53516. Action of **Mg** on β -methyl- γ -bromo- β -butylene (α, β -trimethylvinyl bromide, “ α -methylisocrotyl bromide”) (**I**). **I** reacts with **Mg** like **A**, although not quite so readily. Thus, 200 g. **I**, 30 g. **Mg** and 5 g. **I**, the Et_2O distillate being subsequently treated with **Br**, give 146 g. $\text{Me}_2\text{CBrCHBrMe}$, b_{17} 61–5°. With **HI** gas instead of **Br** the distillate gives **EtI** and Me_3CBrEtI , and with **Na** does not react after 10 hrs. at 100° and 4 hrs. at 160–70°. The residue remaining after distg. the Et_2O , decompd. with cold H_2O and distd. with steam, leaves behind 55 g. of material sepd. by repeated fractionation into a fraction b. 120–5°, with 35.03% **Br**; one (chief fraction) b. 141–4°, with 70.68% **C**, 11.99% **H**, mol. wt. in boiling C_6H_6 133; and a 3rd, b_{18} 91–6°, with 80.46% **C**, 12.06% **H**. All 3 fractions are unsatd., have a pleasant odor and contain **O**. Action of **AcH** on α -methylisocrotylmagnesium bromide. The product is apparently methyl[α, β -dimethyl- α -propenyl]carbinol, an alc. of a very pleasant odor. Action of **Mg** on vinyl bromide. Preliminary expts. show the reaction begins very quickly with evolution of C_2H_2 and C_2H_4 . C. A. R.

Diphenylphosphoric acid as a reagent for the amino group. A. BERTON. *Ber.* 55B, 3361–5(1922).—Diphenylphosphoric acid (**A**) has been found to be a general reagent for the detection of the NH_2 group. $(\text{NH}_2\text{CH}_2\text{CO}_2)_2\text{Cu}$ suspended in PhH and mixed with the equiv. amt. of $(\text{PhO})_2\text{POCl}$ was shaken with H_2O ; the cryst. mass sepd. after 12 hrs. was recrystd. 3 times from EtOH , resulting in large quadratic tables m. 177–8°; the H_2O mother liquor contained only CuCl_2 . The reaction product is a simple salt, $\text{O}:\text{P}(\text{OPh})_2\text{OH} \cdot \text{NH}_2\text{CH}_2\text{CO}_2\text{H}$ (**B**), which was prepd. also by mixing solns. of equiv. amts. of glycolcol and **A**, and evapg. the soln. (cf. Wallach and Heymer, *Ber.* 8, 1236 (1875)). **A** salts were prepd. as well of: *alanine*, voluminous product m. 193°; *leucine*, needles m. 217°; *glutamine*, needles m. 137°; *glycylglycine*, brilliant needles m. 178°; *methylamine*, prepd. by conducting its vapor into a soln. of **A**, thin H_2O -clear, stable tables m. 78–9°; *diethylamine*, made as the preceding compd., small, snow-white crystals, m. 126° after 1 crystn. from H_2O ; and *ammonia*, m. 130°. **A** does not react with amides. For the properties of **A** cf. C. A. 11, 42; *Ann.* 244, 158(1884); 143, 193(1867).

A. R. ALBRIGHT

Preparation of α -trioxymethylene and a new polymericide of formaldehyde. D. L. HAMMICK AND A. R. BOHREX. *J. Chem. Soc.* 121, 2378–40(1922).— α -Trioxymethylene (**A**) was prepd. by modifying Pratesi's method (*Gazz. chim. ital.* 14, 139) as follows: Ten parts paraformaldehyde (**B**) and a mixt. of equal vols. of H_2SO_4 and H_2O (1 part)

were placed at the bottom of glass tubes (18' X 1') and the tubes sealed after exhaustion by the H_2O pump. The lower ends of the tubes were immersed in an oil bath at 115° . After 15 min. the tubes were removed and the portions contg. the long slender needles of **A** were cut off and the crystals scraped out. The yield was about 10%. In using Auerbach and Barschall's method (*Arb. kais. Gesundh.* 27, 220) 40 g. of H_2O should be used per 100 g. **B** (or β - and γ -polyoxymethylenes). The yield is 20%. Upon repeated sublimation of **A** at 46° , it is changed into *ε-trioxymethylene*, large stout prisms, doubly refracting, m. with decompn. and polymerization at 195 – 200° . On heating in an open tube, $HCHO$ is given off and a white sublimate is obtained, m. 163° . It is sol. in boiling $PhNO_2$ and seps. as an amorphous powder. It does not give a Ag mirror with NH_4OH – $AgNO_3$ and could not be acetylated.

C. J. WEST

Hydrolysis of glycine. EMIL BAUR. *Helvetica Chim. Acta* 5, 825–8(1922).—Warburg found that NH_2 acids were oxidized by O in the presence of blood charcoal to CO_2 , NH_3 and H_2O . In the absence of, B. finds that at 40° animal charcoal gradually splits off NH_3 from $H_2NCH_2CO_2H$ (**A**), the amt. formed depending upon the amt. of charcoal and **A** present, upon the time of reaction and the temp. Since the filtrate from the charcoal is neutral, the reaction product must be $HOCH_2CO_2NH_4$. This acid was isolated as the Ca salt.

C. J. WEST

β -Aminodicarboxylic acids and aminopolycarboxylic acids. C. MANNICH AND ERICH GANZ. *Ber.* 55B, 3486–3504(1922).—In contrast to the α - NH_2 acids which have been studied on account of their biological importance, the β -aminodicarboxylic acids (**A**) and β -aminopolycarboxylic acids (**B**) of the acyclic series have been little studied. The synthesis of **A** from monosubstituted malonic acids, CH_2O and N bases takes place with a yield of approx. 70%. The **A** are prepd. by neutralizing half the amt. of monosubstituted malonic acid with the necessary amount of a N base, adding the rest of the malonic acid compd. and finally the required amt. of CH_2O . After standing for several days in the cold the compds. generally cryst. If they do not $EtOH$ or acetone is used to ppt. them. The group substituted in the malonic acid may be Et , allyl, benzyl, γ -phenylpropyl, or phenacyl. Of the bases that may be used, sec. amines give better results than primary amines as the additional H atom of the latter offers a possibility for a reaction with CH_2O . $PhCH_2CH(CO_2H)_2$ gives with NH_3 and CH_2O either $PhCH_2C(CO_2H)_2CH_2NH_2$ (**A**) or the *iminotetracarboxylic acid*, $[PhCH_2C(CO_2H)_2]_2CH_2 \cdot NH$ (**B**). With $PhCH(CO_2H)_2$ a β -aminomonocarboxylic acid is formed, and not an **A**. The **A** are comparatively stable, but when dry gradually decomp. on long standing, giving monobasic α, β -unsatd. acids. The NH_2 acid from $CH_2Et(CO_2H)_2$, CH_2O and $NHMe_2$ gives on boiling in H_2O *ethylacrylic acid*, $EtC(CO_2H) \cdot CH_2$. In the same way by boiling the resp. NH_2 acids α -allylacrylic acid, $CH_2 \cdot CHCH_2C(CO_2H) \cdot CH_2$, ω -phenyl- α -methylenevaleric acid, $PhCH_2CH_2CH_2C(CO_2H) \cdot CH_2$, and α -benzylacrylic acid are formed. By heating β -amino- α -phenylpropionic acid in weak acid soln. atropic acid is formed. α -Benzylacrylic acid on oxidation with $KMnO_4$ gives, besides $BzOH$, α -benzylglyceric acid. The acid from $PhCH_2CH(CO_2H)_2$, CH_2O , and piperidine (a di- CO_2H acid) gives on esterification with alc. and HCl the HCl salt of the *ethyl aminomono-carboxylate*, which on sapon. gives the HCl salt of the acid. [*Methylaminomethyl*]-benzylmalonic acid, $PhCH_2C(CO_2H)_2CH_2NHMe$, gives with $KCNO$ the *ureido acid* $PhCH_2C(CO_2H)_2CH_2NMeCONH_2$, which on heating with xylene splits off CO_2 and forms the monobasic β -[methylureido]benzylpropionic acid, $PhCH_2CH(CO_2H)CH_2NMeCONH_2$. Both urea derivs. form with Ac_2O the same pyrimidine deriv., $PhCH_2CH.CO.NH.CO.NMe.CH_2$. The diamine piperazine (1 mol.) reacts with 2

mols. CH_2O and 2 mols. $CH_2(CO_2H)_2$ with loss of CO_2 , forming a *tricarboxylic acid*, $(HO_2C) \cdot CHCH_2N(CH_2CH_2)_2NCH_2CH_2CO_2H$, which on heating loses CO_2 and gives a

di- CO_2H acid, *piperazine- N,N' -di- β -propionic acid*. Similar to the action of monoalkylmalonic acids with CH_2O , and N bases, forming **A**, an *aminotricarboxylic acid* $(\text{HO}_2\text{C})_3\text{C}(\text{CH}_2\text{NMe}_2)\text{CH}_2\text{CO}_2\text{H}$ may be prepd. from $\text{HO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{H})_2$, CH_2O and NHMe_2 . On boiling the compd. in H_2O it loses CO_2 and gives an aminodicarboxylic acid, $\text{HO}_2\text{C}-\text{CH}(\text{CH}_2\text{CO}_2\text{H})\text{CH}_2\text{NMe}_2$. In place of malonic acids $\text{NCCH}_2\text{CO}_2\text{H}$ may be used with NHMe_2 and CH_2O , forming, $\text{NCCH}_2\text{CH}_2\text{NMe}_2$. The compd. does not ppt. Satg. the soln. with HCl and steam-distg. gives acrylic acid, the nitrile sapon. to $\text{Me}_2\text{NCH}_2\text{CH}_2\text{CO}_2\text{H}$, which in turn gives NHMe_2 and acrylic acid. [*Dimethylaminomethyl*]*ethylmalonic acid* is obtained in 13 g. yield by neutralizing 6.6 g. cooled $\text{EtCH}(\text{CO}_2\text{H})_2$ with 33% NHMe_2 , adding 6.6 g. $\text{EtCH}(\text{CO}_2\text{H})_2$ and 10 cc. CH_2O . Crystals sep. from the cooled soln. and are recrystd. from EtOH . They m. 101° . The H_2O soln. gives off CO_2 at 80° . [*Methylaminomethyl*]*ethylmalonic acid*, prepd. in similar manner with MeNH_2 instead of NHMe_2 , m. 136° . [*Dimethylaminomethyl*]*allylmalonic acid*, obtained in 90% yield from a concd. soln. of NHMe_2 allylmalonate, and CH_2O , forms a slightly sol. double salt with PtCl_4 . [*Dimethylaminomethyl*]*[γ -phenylpropyl]malonic acid* obtained in 7.5 g. yield by neutralizing 3.3 g. $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{H})_2$ with 50% NHMe_2 , adding 3.3 g. more of the above acid and 3 cc. 33% CH_2O , m. 115° . [*Dimethylaminomethyl*]*benzylmalonic acid*, obtained in 90% yield from $\text{PhCH}_2\text{CH}(\text{CO}_2\text{H})_2$, NHMe_2 and CH_2O , m. 88° . [*Piperidinomethyl*]*benzylmalonic acid*, obtained in 85% yield from acid piperidine benzylmalonate (1 mol.) and CH_2O (1 mol.), forms slightly sol. Pb and Ba salts [*Methylaminomethyl*]*benzylmalonic acid*, obtained in good yield at 0° from mol. amts. of acid NH_2Me benzylmalonate and CH_2O , m. 150° . [*Methylureidomethyl*]*benzylmalonic acid* is obtained in 10.2 g. yield by neutralizing 12 g. $\text{PhCH}_2\text{C}(\text{CO}_2\text{H})_2\text{CH}_2\text{NHMe}$ with NaOH , adding an equal amount of NaOH , and 6 g. KCNO , distg. *in vacuo* to dryness after 2 days and acidifying with H_2SO_4 . In 24 hrs. crystals sep., sol in EtOH , m. 98° . β -[*Methylureido*]*benzylpropionic acid*, obtained in 70% yield by refluxing the ureidodicarboxylic acid with 7 parts xylene for 1 hr., crystals from C_6H_6 . *1-Methyl-5-benzyl-2,4-ketohexahydropyrimidine*, obtained in 1.8 g. yield by boiling 3 g. [methylureido]-benzylpropionic acid with 20 cc. Ac_2O for 2 hrs., evapg. on the steam bath to sirupy consistency, dissolving in EtOH and pptg. by pouring into H_2O , needles from C_6H_6 , m. 78° . [*Allylaminomethyl*]*benzylmalonic acid*, obtained from a cold soln. of acid allylamine benzylmalonate (1 mol.) and CH_2O (1 mol.), m. 138° , forms slightly sol. Pb and Ba salts. *Bis-[γ -phenylpropyl]amine- $\beta,\beta,\beta',\beta'$ -tetracarboxylic acid*, obtained in 3.4 g. yield by neutralizing 1 g. $\text{PhCH}_2\text{CH}(\text{CO}_2\text{H})_2$ with NH_3 , adding 5 g. more of the acid, 3 cc. H_2O and 3 cc. CH_2O and letting stand 2 days at 0° , m. 107° . [*Aminomethyl*]*benzylmalonic acid*, obtained from $\text{PhCH}_2\text{CH}(\text{CO}_2\text{H})_2$, NH_3 , and CH_2O , m. 148° . α -*Phenyl- β -dimethylaminopropionic acid*, obtained from $\text{PhCH}_2\text{CH}(\text{CO}_2\text{H})_2$, NHMe_2 and CH_2O , m. 143° . β,β' -*Iminobis-[α -phenylpropionic acid]*, prepd. from 3.6 g. $\text{PhCH}_2\text{CH}(\text{CO}_2\text{H})_2$, 1 g. NH_4Cl and 2 cc. CH_2O (yield 2.2 g.), m. 112° . [*Dimethylaminomethyl*]*phenacylmalonic acid*, obtained in 45% yield from 1 mol. acid NHMe_2 phenacylmalonate and 1 mol. CH_2O , m. 148° . *Piperazine- N - β -propionic acid- N' - β' -isosuccinic acid*, obtained in 4.6 g. yield from 10.4 g. malonic acid, 8.6 g. piperazine, and 20 cc. CH_2O (33%), m. 227° . *Piperazine- N,N' -di- β -propionic acid*, obtained in 5.8 g. yield by adding HCl to the mother liquor from the preceding compd., concg. on the steam bath and cooling, m. $261-2^\circ$. β,β -*Dicarboxy- γ -dimethylaminobutyric acid*, prepd. from $\text{HO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{H})_2$, NHMe_2 and CH_2O , m. 135° . β -*Carboxy- γ -dimethylaminobutyric acid*, obtained from the preceding acid by boiling with H_2O (CO_2 is evolved), evapg. to a sirupy consistency and pptg. with abs. EtOH . C. T. WHITE

A synthesis of aminohydroxydicarboxylic acids. C. MANNICH and M. BAUROT. *Ber.* 55B, 3504-9(1922).—Aminohydroxydicarboxylic acids are obtained by allowing a concd. soln. of the acid amine salt of tartaric acid (**A**) to react several days in the cold

with the theoretical amt. of CH_2O . The compds. gradually crystallize. They are unstable, and give off CO_2 . [Dimethylaminomethyl]lartronic acid (B) decomps. in H_2O , giving partly CO_2 , NHMe_2 and pyrrolacemic acid, $\text{CH}_2\text{:C(OH)CO}_2\text{H}$, and partly CO_2 and *N*-dimethyl-*dl*-serine, $\text{HO}_2\text{CCH(OH)CH}_2\text{NMe}_2$. B₁ is obtained in 6 g. yield by exactly neutralizing 3.6 g. A in 1.5 g. cold H_2O with 50% NHMe_2 , adding 3.6 g. A and finally 6 g. CH_2O soln. After standing for 3 days the crystals are filtered and washed with MeOH. [Methylaminomethyl]lartronic acid, obtained in 3.8 g. yield by neutralizing 4.2 g. A in 2 g. cold H_2O with 40% MeNH_2 , then adding 4.2 g. A and finally 6.2 cc. 35% CH_2O , decomps. 153° . [Aminomethyl]lartronic acid is prepd. in similar manner from A, NH_3 and CH_2O . [Piperidinomethyl]lartronic acid is obtained in 1.5 g. yield by neutralizing 3.6 g. A in 1.5 g. H_2O with piperidine, adding 3.6 g. A more and finally 5.4 cc. CH_2O soln. After 3 days standing the compd. is pptd. by adding 75 cc. abs. EtOH and gradually 150 cc. of acetone. It decomps. 190° . The above compds. are only slightly sol. in MeOH, EtOH, and acetone.

C. T. WHITE

Some derivatives of diethylmalonic acid. P. DUMESNIL. *Bull. soc. chim.* 31, 687–9(1922).—The action of SOCl_2 on $\text{C}_2\text{H}_5(\text{CO}_2\text{H})_2$ produces an acid chloride and an anhydride. This has been attributed to impurities in the SOCl_2 but D., using a specially purified product, found the proportion of chloride and anhydride unchanged.

JAMES A. BRADLEY

Syntheses of alkylidenecyanoacetic acids and of substituted succinic acids. II. Preparation of acids containing saturated aliphatic residues and the constitution of the aliphatic alkylidenecyanoacetic esters. ARTHUR LAPWORTH AND J. A. McRAE. *J. Chem. Soc.* 121, 2741–57(1922); cf. *C. A.* 16, 4197.—No definite products could be isolated from the reaction of $\text{C}_6\text{H}_{13}\text{CHO}$ or AcH with $\text{NCCHNaCO}_2\text{Et}$. The action of KCN and AcOH upon the product from $\text{C}_6\text{H}_{13}\text{CHO}$ gave a 60% yield of $\text{HO}_2\text{CCH}(\text{C}_6\text{H}_{13})\text{CH}_2\text{CO}_2\text{H}$ (A), the imide of which forms clusters of silky needles, m. 91° . With AcH , 40–50% yields of $\text{HO}_2\text{CCHMeCH}_2\text{CO}_2\text{H}$ were obtained. Very small yields of substituted succinic acids were obtained from ketones through the above reaction. The following reactions and properties of $\text{C}_6\text{H}_{13}\text{CH}_2\text{C(CN)CO}_2\text{Et}$ are reported: It reacts very slowly with Br at room temp.; boiled with EtOH-KOH it gives NH_3 and $\text{C}_6\text{H}_{13}\text{CHO}$. It is sol. in NaHSO_4 and in concd. soln. the additive compd. is salted out as an oil; the esters have not been regenerated from this compd. The ester is also sol. in aq. KCN and the crude oil which ppts. on addn. of acid yields 85% of A. EtONa in EtOH gives a golden yellow soln. The ester reacts slowly with O_3 , the 1st portion of the distillate contg. $\text{C}_6\text{H}_{13}\text{CHO}$. Heated with PhCH_2Cl and EtONa, a mixt. of $\text{C}_6\text{H}_{13}\text{CH}_2\text{CHC}(\text{CH}_2\text{Ph})(\text{CN})\text{CO}_2\text{Et}$ and $\text{C}_6\text{H}_{13}\text{CH}_2\text{CHCH}(\text{CH}_2\text{Ph})\text{CN}$ is obtained. $(\text{CH}_3)_3\text{C:C(CN)CO}_2\text{Et}$ is sol. in aq. KCN or NaHSO_4 and reacts slowly with Br and O_3 . In the latter case cyclohexanone was isolated from the distillate. KCN gives *1*-carboxycyclohexyl-*1*-acetic acid, plates, m. 132° . These facts point to the α,β -type of unsatd. esters.

C. J. WEST

Conditions underlying the formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. V. Products derived from α -halogenated β -methylglutaric acids. C. K. INGOLD. *J. Chem. Soc.* 121, 2676–95(1922).—I. makes an exptl. comparison between glutaric acid (A) and its β -Me (B) and β,β -Me₂ (C) derivs. with respect to the manner in which the ease of their transformation into cyclic structures by the interaction of substituents attached to 2 AcOH residues is conditioned by the angles between these groups. The proportions of hydroxylation products to ring-acids calcd. as % of the material identified as having passed into one or the other of these 2 forms are: A 25, 75; B 11, 89; C, 5, 95. These figures show the effect of introducing 1 and then a 2nd β -Me group into derivs. of A on the ease of their transformation into acids of the cyclopropane series. Methyl α -bromo- β -methyl-

glutarate, b_{12} 143-5°. α -Iodo derivative, b_{12} 180°. Ethyl ester, b_{10} 199-200°. α, α' -Dibromo- β -methylglutaric acid, A form (D), dense, strongly refracting prisms, $m.$ 153-4°, obtained by pouring the reaction mixt. into HCO_2H and as the C_6H_6 -insol. portion; the B form (E) seps. from the C_6H_6 mother-liquors as microneedles, $m.$ 116-8°. Methyl ester, b_{25} 179-80°; ethyl ester (F), b_{28-30} 189-90°. When $\text{EtO}_2\text{CCHBrCHMeCH}_2\text{CO}_2\text{Et}$ was boiled with 4.5 equivs. 2 N Na_2CO_3 for 20 hrs., the product acidified and extd. with Et_2O , the following products were isolated: α -hydroxy- β -methylglutaric acid lactone (G), viscous liquid, b_{25} 189-90°; ammonium salt, rosetts of needles; silver salt, needles; barium salt of the acid (which is not stable in the free state), leaflets which disintegrate on drying at 120°; silver salt. The other product was *trans*-3-methylcyclopropane-1,2-dicarboxylic acid (J. prakt. Chem. [2] 68, 159), the calcium salt of which forms small leaflets; silver salt. The anhydride of the *cis*-acid was obtained by heating the *trans*-acid with Ac_2O at 180° for 6 hrs., $b.$ 270°. Calcium salt of *cis*-acid, small leaflets; silver salt. The reaction product with 6 N MeOH-KOH was fractionated as the benzyl esters. The more volatile esters contained G, the *di-p*-toluidide of which forms leaflets, $m.$ 235-6°, methylitaconic acid, and methylparaconic acid. The less volatile benzyl esters gave, on hydrolysis, methylitaconic acid, ethylmalic acid (H), and 3-methylcyclopropane-1,2-dicarboxylic acid and B. Hydrolysis of D by boiling with 2 N aq. Na_2CO_3 for 1.5 hrs. gave *A*- α, α' -dihydroxy- β -methylglutaric acid lactone, short, stout rhombic prisms, $m.$ 136-6.5°; this was also obtained in considerable yield by the hydrolysis of E. The free acid crystallizes in plates, $m.$ 80° to give the lactone; barium salt, leaflets; silver salt. *Di-p*-toluidide, needles, $m.$ 207°. *B*-Lactone, minute granules from Et_2O , $m.$ 117-8°. *B*-acid, stable only as a salt; barium salt, minute rosetts of needles; silver salt; *di-p*-toluidide, long needles readily sol. in EtOH (distinction from the A-deriv.), $m.$ 187°. Hydrolysis of the Me or Et esters gave the A- and B-acids; 1-bromo-3-methylcyclopropane-1,2-dicarboxylic acid, $m.$ 190-1°; this is stable towards alk. KMnO_4 and does not show the presence of Br with HNO_3 and AgNO_3 . Silver salt, very stable. Boiled with 2 N Na_2CO_3 for 1 month, the Br acid gave the 1-hydroxy derivative, microneedles, $m.$ 167-9°; it is stable towards boiling HCl , dil. alkalis and cold alk. KMnO_4 . Silver salt.—With 6 N MeOH-KOH , F gave the A- and B-acids, methyleyclopropene-dicarboxylic acid, 1-methoxy-3-methylcyclopropane-1,2-dicarboxylic acid, needles, $m.$ 102-4°, and butane- α, γ -diol- α, β -dicarboxylic acid lactone, obtained only as a viscous gum. Calcium salt; barium salt, microneedles. Ethyl ester, b_{25} 168-71°. Silver salt.—The lactonic acid was reduced by boiling 24 hours with an excess of distd. HI to H and ethylsuccinic acid.

C. J. WEST

Preparation of β -hydroxy- α -amino acids from olefinic carboxylic acids. WALTHER SCHRAUTH AND HANNO GELLER. Ber. 55B, 2783-96(1922).—In view of the possibility that there may be present in proteins β -hydroxy- α -amino acids, other than serine, which may not be able to withstand the usual methods of isolation, any general method for the prepn. of such acids would be of great physiol. and chem. interest. The various methods by which serine has hitherto been prepd. are not of general applicability. S. and G. hoped such a general method might be based on the property of α, β -olefinic carboxylic esters of reacting with Hg^{++} salts in alc., the Hg salt residue adding at the double bond in the α -position and an alkoxy group in the β -position (C. A. 4, 1310); the Hg in the resulting compd. should be replaceable by halogen and the compd. so obtained, should, after hydrolysis of the ester, give with NH_3 the β -alkoxy- α -amino acid which, dealkylated with HBr or HI , ought to yield the desired β -hydroxy- α -amino acid. $\text{Me}_2\text{C}(\text{CHCO}_2\text{Et})_2$ reacts quite sluggishly with $\text{Hg}(\text{OAc})_2$ in MeOH , 72 hrs. being required for completion of the reaction, but addn. of KBr to the mixt. gives ethyl β -methoxy- α -bromo-mercuriovalerate (A) in 70% yield; this, with 2 mols. Br in CHCl_3 , gives after 4-7 days ethyl β -methoxy- α -bromoisovalerate (B), sapond. by shaking with dil. NaOH at room temp.

to the acid (C) (yield, 70%), which with aq. NH_4OH at 100° gives 74% *dimethylserine methyl ether* (D), from which the *dimethylserine* (E) is easily obtained in 71% yield by boiling with HBr . With $\text{PhCH:CHCO}_2\text{Me}$, the addn. of $\text{Hg}(\text{OAc})_2$ takes place more rapidly (12 hrs.) and treatment with KBr gives a good yield of *methyl β -phenyl- β -methoxy- α -bromomercuri- β -propionate* (F). The velocity of the elimination of the Hg from F and the yield of the product depend materially on the solvent; in CHCl_3 2-3 days are required while in AcOEt the reaction is complete in 1 hr.; in CHCl_3 there is also always formed simultaneously *methyl β -phenyl- α,β -dibromopropionate* (G), m. 117° , as a by-product, while in AcOEt only the expected *methyl β -phenyl- β -methoxy- α -bromopropionate* (H) (yield, 91%) is obtained and is hydrolyzed to the free acid (I) with NaOH at room temp. Even by using halogen acids instead of NaOH , however, the yield of I cannot be raised above 56%, with HBr were always formed considerable amts. of *β -phenyl- α,β -dibromopropionic acid* (J), with alkalies Br -free sapon. products. To avoid the necessity of hydrolyzing the product, therefore, free $\text{PhCH:CHCO}_2\text{H}$ was mercurated, giving 92% of *β -phenyl- β -methoxy- α -bromomercuri- β -propionic acid* (K), which with Br yielded 65% of an acid (L), not identical but apparently stereoisomeric with I. From the *β -phenyl- β -methoxy- α -aminopropionic acid* (M), obtained without difficulty from L, the Me group could not be removed with either HBr or HI , the product always being bromohydrocinnamic acid, with traces of $\text{PhCH:CHCO}_2\text{H}$, the scission of the ether residue apparently being sterically hindered (at least in the particular stereoisomeric form used in this instance). *p*- $\text{MeOC}_6\text{H}_4\text{CH:CHCO}_2\text{Et}$ likewise adds $\text{Hg}(\text{OAc})_2$ rapidly (12 hrs.) and ethyl *β -p-methoxyphenyl- β -methoxy- α -bromomercuri- β -propionate* (N) is obtained in 90% yield; with Br , however, with which it reacts with evolution of much heat, it does not give the desired α - Br ester but chiefly (93%) ethyl *β -[p-methoxybromophenyl]- β -methoxy- α -bromopropionate* (O), which on hydrolysis and treatment with NH_4OH yields the α -amino acid (P). To prevent this unexpected entrance of the Br into the nucleus the *iodo analog* (Q) of N was prep.; this reacted exceedingly slowly (3 days) with 2 mols. I , giving the desired ethyl *β -p-methoxyphenyl- β -methoxy- α -iodopropionate* (R), which with dil. NaOH at room temp. gave the free acid (S); this, however, could not be converted into the amino acid (T) with aq. or liquid NH_3 , on heating or at room temp.; $\text{MeOC}_6\text{H}_4\text{CH:CHCO}_2\text{H}$ was always regenerated and partially decompd. into CO_2 and $\text{MeOC}_6\text{H}_4\text{CH:CH}_2$; only in one case was the desired T obtained and then in exceedingly small yield. The above results indicate that the suggested method will yield good service in the purely aliphatic series but that a β -Ph residue may sterically hinder the smooth scission of an ether grouping on the same C atom. A, plates from alc., m. 51° . B (yield, 73%), oil of sharp odor. C, purified by pptn. from Et_2O with petr. ether, m. 77° . *β -Methoxy- α -aminoisovaleric acid* (D), plates from dil. alc., decomp. 250 - 60° . *α -Hydroxy acid* (E), plates from H_2O - EtOH , m. 218° (decompn.), has a sweet taste; phenyl isocyanate, m. 162° (gas evolution); *β -naphthalenesulfonyl derivative* (yield, 96%), needles from alc., m. 261° . K, flocks, m. 160 - 6° (decompn.). L begins to sinter 165° m. clear 170° . M (yield, 66%), elongated plates from 30% alc., m. 236° (gas evolution); phenyl isocyanate, plates from H_2O , m. 161° (gas evolution); *β -naphthalenesulfonyl derivative*, prisms from H_2O , m. 157° . I, needles from AcOEt -petr. ether, m. 126 - 7° . N, prismatic plates from alc., m. 107° . P, long, faintly yellowish plates from H_2O , m. 224° (decompn.); phenyl isocyanate. Q, m. 117° . R (yield, 71%), faintly yellowish oil. S, needles with $2\text{H}_2\text{O}$ from Et_2O -petr. ether (yield, 61%), m. 89 - 90° . T, long plates from dil. alc., m. 233° (decompn.).

C. A. R.

Synthesis of hydroxyamino acids, and of an amino acid from methyl cyclopropyl ketone ("acetyltrimethylene"). N. D. ZELINSKII AND E. F. DENGIN. *Ber.* 55B, 3354-61 (1922).—To provide means for the better identification of NH_2 acids obtained from albumins by hydrolysis, a no. of hydroxyamino acids were synthesized, using Z.

and Stadnikoff's cyanohydrin method (*Ber.* 39, 1722(1906)), starting with keto alcs. α -Amino- α -methyl- β -hydroxypropionic acid (A) was prep'd. from either acetylcarbinol acetate (B) or acetylcarbinol (C). B was made (Perkin, *J. Chem. Soc.* 59, 786(1891)) by warming a mixt. of AcOK and abs. EtOH, and slowly adding ClCH_2COMe ; yield, 60% of the theoretical, b. $174-5^\circ$, b_{18} 82° . C, prep'd. by warming B in H_2O with BaCO_3 , b_{18} $55-60^\circ$. To 6.5 g. KCN and 5.3 g. NH_4Cl in 30 cc. H_2O was added with cooling 11.5° g. B; after standing 1 hr. at a low temp., 17 hrs. without cooling, and 6 hrs. at $40-2^\circ$, 1 vol. of fuming HCl was added to the cooled mixt. which was then sat'd. with HCl gas. After 24 hrs. 1 vol. H_2O was added and the mixt. warmed 2 hrs., then evap'd. to dryness on a H_2O bath, and ext'd. with boiling abs. EtOH. The residue from the evap'n. of the EtOH was taken up with H_2O and the soln. treated with freshly ppt'd. Pb(OH)_2 ; the filtrate was treated with H_2S , filtered, conc'd. to 30 cc., dried in a vacuum desiccator, and triturated with abs. EtOH; A was thus obtained as a white powder which on crystn. from dil. EtOH formed small transparent tables sol. in H_2O , insol. in abs. EtOH, m. in a sealed tube 243° (decompn.); yield, 12.6% of the theoretical. The copper salt ($\text{C}_4\text{H}_7\text{O}_3\text{N}_2$) \cdot $\text{Cu}\cdot 2\text{H}_2\text{O}$, prep'd. by boiling A in H_2O with CuCO_3 , forms small blue needles, easily sol. in H_2O . A was prep'd. from C in the same way as from B. A is isomeric with 3 acids which are described. Hydroacetylacetone (D) was prep'd. (Claisen, *Ber.* 25, 3164(1892); *Ann.* 306, 322(1899)) from AcH and Me_2CO in the presence of KCN; after fractionating in a vacuum it b_{17} 76° . α -Amino- α -methyl- γ -hydroxyvaleric acid (E) was prep'd. by adding 15.3 g. D to 9.75 g. KCN and 8.03 g. NH_4Cl in 45 cc. H_2O , with cooling; the resulting emulsion was treated as in the prepn. of A; yield, 25% of the theoretical. E crysts. from H_2O or EtOH- H_2O in needles, m. $232-3^\circ$; the copper salt ($\text{C}_6\text{H}_{11}\text{O}_5\text{N}_2$) \cdot $\text{Cu}\cdot 2\text{H}_2\text{O}$, prep'd. by boiling E with CuCO_3 , is cryst., and sol. in H_2O and abs. EtOH. γ -Acetopropyl alcohol (F) was prep'd. (Lipp, *Ber.* 22, 1196(1889)) by dissolving 100 g. Na in 1040 g. abs. EtOH, treating with 520 g. $\text{AcCH}_2\text{CO}_2\text{Et}$, adding 744 g. $(\text{CH}_3)_2\text{Br}_2$ and refluxing the mixt. 10 hrs. on a H_2O bath; after taking up with H_2O , 800 g. of oily product remained, which was refluxed 16 hrs. with 245 g. HCl, (d. 1.1), and 1240 cc. H_2O ; the soln. was salted with K_2CO_3 , and the product dried with fused K_2CO_3 . After distg. the EtOH, F was rectified in a vacuum; yield, 125 g. (50% of the theoretical), b. $122-3^\circ$; l.'s yield was 80-88 g. α -Amino- α -methyl- δ -hydroxyvaleric acid (G) was obtained in low yield by treating 6.5 g. KCN and 5.15 g. NH_4Cl in 35 cc. H_2O at low temp. with 10.2 g. F; the reaction mixt. was worked up as with A. G is sol. in H_2O , insol. in abs. EtOH, crysts. from dil. EtOH in small needles, m. $198-200^\circ$; it has a sour taste. G gradually loses wt. at 100° , perhaps because of lactone formation; the copper salt, ($\text{C}_6\text{H}_{11}\text{O}_5\text{N}_2$) \cdot Cu , was obtained in cryst. form by taking up the original sirup with abs. EtOH, distg. the solvent in a vacuum, and rubbing the residue with abs. Et $_2\text{O}$; it forms granular masses, partially decomp. at 100° . 2 isomers of E and G are noted, with references. δ -Acetobutyl alcohol (H) was made (Lipp, *Ann.* 289, 181(1896)) from $\text{AcCH}_2\text{CO}_2\text{Et}$, $\text{CH}_2(\text{CH}_2\text{Br})_2$ and EtONa in 36% yield; it b_{14-5} $111-3^\circ$. α -Amino- α -methyl- ϵ -hydroxycaproic acid (I) was prep'd. from 18 g. H, 9.8 g. KCN and 8.0 g. NH_4Cl in the same way as A, E, or G, in 20% yield of cryst. product; it seps. from H_2O in small tables m. $224-6^\circ$. The copper salt, ($\text{C}_7\text{H}_{14}\text{O}_5\text{N}_2$) \cdot $\text{Cu}\cdot 2\text{H}_2\text{O}$, is obtained as a blue cryst. powder by dissolving in abs. EtOH and evapg. the solvent. Acetyltrimethylene (J) was made (Wagner, *J. Russ. Phys. Chem. Soc.* 30, 261(1898)) by slow addn. of $\text{Ac}(\text{CH}_2)_3\text{Cl}$ (b_{10} $71-2^\circ$) to powdered KOH; H_2O was added, the mixt. heated gently for 2 hrs., and distd.; the product was salted out with K_2CO_3 and dried; yield, 70 g., b. 113° , from 166 g. chloride, or 80% of the theoretical. A mixt. of 8.4 g. J, 6.5 g. KCN, 5.15 g. NH_4Cl and 30 cc. H_2O was shaken 20 hrs. and then ext'd. with Et $_2\text{O}$. Hydrolysis of the extd. nitrile with HCl yielded the cryst. hydrochloride of methylcyclopropylaminoacetic acid (K); K was isolated by boiling with freshly ppt'd. Pb(OH)_2 and removal of Pb with H_2S ; it crystallizes in needles easily

sol. in H_2O and $EtOH$, tastes sweetish and has an odor of milk, m. in a sealed tube $273-5^\circ$ without decompn., begins to sublime at 110° ; the copper salt has $2H_2O$.

A. R. ALLBRIGHT

An attempt to prepare carbonyl cyanides and a method to obtain unsaturated amino acids. O. DIELS, H. GÄRTNER and R. KAACK. *Ber.* 55B, 3439-48(1922).—Attempts to prep. *mesoxalic nitrile*, $OC(CN)_2$ from hydroxymethylenemalonic nitrile, $HOCH:C(CN)_2$ and O_3 under varying conditions were unsuccessful. In efforts to obtain *ethyl mesoxalate nitrile*, $CNCOCO_2Et$, from $EtOCH:C(CN)CO_2Et$ and O_3 , HCN and $(CO_2H)_2$ were the only products obtained. The hydroxymethylene combinations of malonic nitriles and cyanoacetic esters react with amines, forming combinations which can be utilized for the synthesis of unsatd. NH_2 acids. $HOCH:C(CN)CO_2Et$ gives with $PhCH_2NH_2$ and $PhNH_2$ combinations which on sapon. yield β -benzylamino- and β -anilinoacrylic acids, resp. [*Ethoxymethylene*]malonic nitrile, obtained in 28 g. yield by refluxing 20 g. $CH_2(CN)_2$, 46 g. $HC(OEt)_3$ and 80 cc. Ac_2O for 7 hrs., evap. to $1/2$ the original vol. and allowing to stand 24 hrs. over soda lime and recrystg. the crude product from C_6H_6 and then from alc. (yield, 20 g.), m. 65° . 1,3-Dimethylcyclobutane-2,2,4,4-tetranitrile, obtained by mixing 5 g. $CH_2(CN)_2$, 4 g. AcH , and 3 g. piperidine at 0° , heating until a sirupy mass forms, cooling to 0° for 3 hrs., warming on a steam bath until crystals form and recrystg. from $EtOH$ and $AcOH$ (yield 2.53 g.), m. $184-5^\circ$. Methylenebimalonic nitrile, obtained in 1.5 g. yield from 4 g. $CH_2(CN)_2$ in $EtOH$ and 2.32 g. 40% formalin at 0° , prisms from $MeCN$ and C_6H_6 , m. 136° . β -Benzylaminoacrylic acid is prepd. from 23 g. Et [benzylaminomethylene]cyanoacetate, 300 cc. 96% $EtOH$ and 4.6 g. Na in 100 cc. $EtOH$ refluxed on a water bath for 28 hrs. The ppt. which forms during the refluxing is filtered off, dissolved in H_2O , made slightly acid with $AcOH$, and extd. with ether, and the ether ext. fractioned under vacuum. The crude product b_{11} $105-6^\circ$. Recrystd. from $MeCN$, it m. $97-8^\circ$. β -Anilinoacrylic acid is obtained only in poor yield by refluxing on the water bath 21.6 g. Et [anilinomethylene]cyanoacetate, 150 g. $EtOH$ (96%) and 4.6 g. Na in 100 cc. $EtOH$, extg. with ether, distg. off the ether and recrystg. the Na salt from alc. Ethyl [hydrazinomethylene]cyanoacetate is obtained by mixing 6 g. cooled $EtOCH:C(CN)CO_2Et$ with the mol. amt. of $N_2H_4 \cdot H_2O$ and warming until a yellow soln. forms which on cooling gives an amorphous mass. Many recrystns. from $EtOH$ give white needles, m. $96-7^\circ$. C. T. W.

[*Ethoxymethylene*]diacetyl and ϵ -ethoxy- β,γ -pentanedione. O. DIELS and J. PETERSEN. *Ber.* 55B, 3449-57(1922).—[*Ethoxymethylene*]diacetyl (A), $EtOCH:CH-COCOME$, obtained by refluxing 60 g. Ac_2 , 100 g. $HC(OEt)_3$, and 200 g. Ac_2O for 20 hrs. and distg. the product in a vacuum (yield, 7-8 g.), b_{10} $85-6^\circ$. The sapon. of A to an unsatd. diketose has not been successful owing to instability of the latter. By heating 2 g. A with 3 g. $o-C_6H_4(NH_2)_2$ in 10 cc. pyridine and cooling the quinoxaline $H_2NC_6H_4NHCH:CHC:N.C_6H_4.N.CMe$ seps. Recrystd. from pyridine (yield, 1.1 g.),

it m. 183° . A forms a monoanil-anilide and monophenylhydrazone with $PhNH_2$ and $PhNHNH_2$. By mixing 1.42 g. A in 2 cc. $MeCN$ with 1.92 g. $PhNHNH_2$ in 3 cc. $MeCN$ there is formed a pyrazole $PhNHN:CMcC:N.NPh.CH:CH$, yellow plates from $MeCN$

(yield 0.31 g.), m. 182° . On ozonizing 2 g. A in 8 cc. dry $CHCl_3$ for 1.5 hrs., and distg. off the $CHCl_3$, there remains an oil, α,β -diketobutyraldehyde, which on treating in cold H_2O with 1.5 g. $o-C_6H_4(NH_2)_2$ gives quinoxaline, $H_2NC_6H_4N:CHC:N.C_6H_4.N:NMe$,

m. 166° . A is hydrogenated without difficulty in the presence of colloidal Pd , giving ϵ -ethoxy- β,γ -pentanedione. An unsatd. ketone, $MeC(:NOMe)COCH:CMcC(:NOMe)Me$ may be formed by adding slowly to 34 g. $NaOEt$ in 10 parts abs. ether with cooling, a mixt. of 50 g. $AcC(:NOMe)Me$ and 37 g. acid-free, dry HCO_2Et . After standing 1 hr.

a part of the reaction product is treated with ether, made acid with H_2SO_4 and the ether distd. off. The oily residue b₁₁ 120-6° (decompn.), gradually crystallizes and m. 50°. The other part of the reaction product, after standing 15 hrs. with cooling, and evap. off the ether, yields hexagonal plates from EtOH, m. 138°. C. T. WHITE

The preparation of aromatic α -ketonic acids. RAGNAR SÖDERQUIST. *Svensk. Kem. Tids.* 34, 188-92(1923).—A review. A. R. ROSE

Barbituric acid. WALTER BOCK. *Ber.* 55B, 3400-5(1922).—Barbituric acid (A), even in 1:10000 diln. and in the presence of free acids, colors wood a bright yellow-red, and paper from wood pulp yellow. Substitution in the 5-position destroys this property. *Monobromobarbituric acid* (B) can be directly prepd. by adding 0.8 mol. Br_2 to A in H_2O at 50-60°, needles on cooling (70% yield), m. 212-5° with preliminary sintering, identified with Baeyer's product by prepn. of the NH_4 salt. On addn. of Br_2 it forms 5,5-dibromobarbituric acid, both (forms plates (C), decomp. 235-7°, and prisms (D), decomp. 220-1°), being isolated. Each, on standing with Br water, gives tribromoacetylurca, and each with KI forms K barbiturate, (identified by the wood test). D, by the action of Br_2 forms also benzalbarbituric acid, which, refluxed 1 hr. with 2 parts Br_2 in MeOH, again forms D. B, boiled in H_2O for 45 min., is completely decompd. A, identified by the wood test, and hydruilic acid, were isolated; parabanic acid could not be isolated. C, heated in H_2O 45 min., showed traces of alloxan (E); after 1.5 hr., large amts. of E; after 2.5 hrs. a color change indicated a secondary reaction, yielding A (traces) and hydruilic acid. The neutral salts of B are stable; this may indicate that the speed of the decompn. is a function of the acidity. A couples with quinone (F), even in 1:10000 diln. A stable product is formed, however, only when 1 mol. A and 2 mols. F are refluxed 1 hr. in H_2O . Cooling ppts. a dark green amorphous substance, $\text{C}_{22}\text{H}_{20}\text{O}_{12}\text{N}_4$, which decomps. without melting. From H_2O , $\text{Ba}(\text{OH})_2$ ppts. a brown powder, $(\text{C}_{22}\text{H}_{17}\text{O}_{12}\text{N}_4)_2\text{Ba}_3$. I. P. ROSE

Reduction of lignin and of carbohydrates with hydriodic acid and phosphorus. R. WILSTÄTTER AND L. KALB. *Ber.* 55B, 2637-52(1922).—Lignin with boiling HI and P passes through black-brown intermediate stages into a colorless resin of weakly acid nature, easily sol. in alc. and AcOH; at higher temps. under pressure the reaction proceeds further, again with the formation of a weakly acid substance of high mol. wt. sol. in gasoline and Et_2O ; the final product is a mixt. of hydrocarbons which can be sepd. into a liquid portion easily sol. in Me_2CO and a solid part difficultly sol. in Me_2CO . The hydrocarbon mixt. has the mean compn. $\text{CH}_{1.4}$; the liquid part is somewhat richer, the solid part somewhat poorer in H. The liquid part has d. 0.9-1.0. The lowest mol. wt. is 167, the highest (of the solid part) 842. Both mixts. form a related, analogous (not homologous) series whose properties recall those of hydroaromatic hydrocarbons. The same substances were obtained in the same way from carbohydrates; not, however, by way of the known transformation of hexitol into iodohehexane, which does not give the hydrocarbon mixt. But hexitol directly, glucose, xylose and cellulose give mixts. of similar properties; the analogy extends to the formation of the weakly acid substance and another, insol. in all solvents. Xylose and cellulose yield the products of high mol. wt. in greater abundance than glucose or hexitol; they are also obtained in large amt. from the humin-like substance formed by decompn. of glucose with HCl. Since the reduction products are not formed through hexyl iodide from the carbohydrates there must be another reactive intermediate product which is capable of polymerization through C condensation. That this polymerization stops at stages of the most widely varying mol. wts. may be due to the fact that it can be interrupted at all stages by the simultaneous progressive hydrogenation which results in the formation of highly hydrogenated, no longer alterable hydrocarbons. Such intermediate products are probably furan derivs., possibly also diolefins. The fact that lignin, the humin-like substance and

cellulose yield the products of higher mol. wt. in larger amt. than glucose might be explained by the assumption that the intermediate product in question is to a larger or smaller extent preformed in the former substances while glucose is for the most part converted into hexyl iodide on even gentle warming with the reducing agent; the intermediate product, once formed, can no longer be converted into hexyl iodide on mild treatment with the reducing agent but under more drastic conditions gives the products of high mol. wt. In the case of lignin, the humin-like substance and cellulose it is not necessary to assume a preliminary profound degradation. As to what ring systems are formed in the polymerization, it may be assumed, as long as the nature of the hydrocarbon mixt. is not clearly known, that, in view of the isomerizing influence of the HI, the end product will contain 5- and 6-membered rings, as being the most stable. These results indicate that there is a close constitutional relationship between lignin and carbohydrates. The lignin was obtained in 26-8% yield from pine, 23% from beech sawdust, by adding 200 g. of the sawdust (previously purified by successive extrn. with H_2O , 80 and 100% Me_2CO) to 4 l. concd. HCl, letting stand 4 hrs. with occasional shaking, stirring into 1300 g. crushed ice, dilg. after 18 hrs. with 1300 cc. H_2O , washing with 1:1 HCl, then with H_2O , boiling up with 8 l. of H_2O cautiously neutralizing with Na_2CO_3 and repeating the boiling with pure H_2O one or more times. So obtained, the lignin is of a light brownish color, Cl-free, still contains a small amt. of substances which can be converted into sugar and has 1.3% ash. Below are the % of Et_2O -insol. residue, total hydrocarbons, liquid hydrocarbons and solid hydrocarbons, resp., obtained with HI-P from the various substances studied: pine lignin 23, 28, 16, 10; beech lignin 23, 32, 15, 17; humin-like substance, 47, 20, 10, 10; cotton 9, 20, 8, 12; glucose, 3, 17, 11, 4; xylose 14, 16, 8, 7; mannitol, 3, 16, 12, 3.

C. A. R.

Structure of fucose. E. P. CLARK. *Bur. Standards, Sci. Papers* No. 459, 527-34 (1922).—This article, similar in text to C. A. 16, 4190, establishes in a practical way the conclusions regarding the configuration of fucose established theoretically by Hudson (C. A. 4, 1466; 5, 1738).

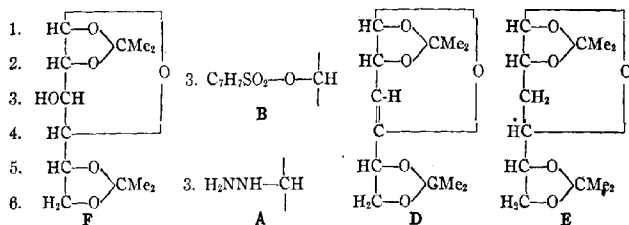
T. SWANN HARDING

Glucosides. XI. Glucosides of glycerol. P. KARRER and O. HURWITZ. *Helvetica Chim. Acta* 5, 864-9 (1922); cf. C. A. 16, 1745.—1-Tetraacetyl-d-glucosidoacetoneglycerol (A) results by the action of acetobromoglucose upon glycerolacetone in the presence of Ag_2CO_3 , in 67% yield; cryst., m. 132° , $[\alpha]_D^{20} -20.77^\circ$ ($CHCl_3$). Careful sapon. of A with $EtOH-H_2SO_4-H_2O$ at $45-48^\circ$ gives 1-tetraacetyl-d-glucosidoglycerol (B), in 60% yield, which forms a pulverizable mass, but which is reconverted into cryst. A upon shaking with AcMe containing 0.6% HCl. Ac_2O and $AcONa$, acting upon B, give 2,3-diacetyl-1-[tetraacetyl-d-glucosido]glycerol (78% yield), cryst., m. 98° , $[\alpha]_D^{20} -30.96^\circ$ ($EtOH$), which, sapond. with $Ba(OH)_2$ at room temp. for 24 hrs., yields 1-d-glucosidoglycerol, amorphous mass, $[\alpha]_D^{18} -27.72^\circ$. This is decompd. by emulsion with the formation of glucose. This appears to be identical with the compd. prepd. by biochem. synthesis (C. A. 9, 2521, 2639).

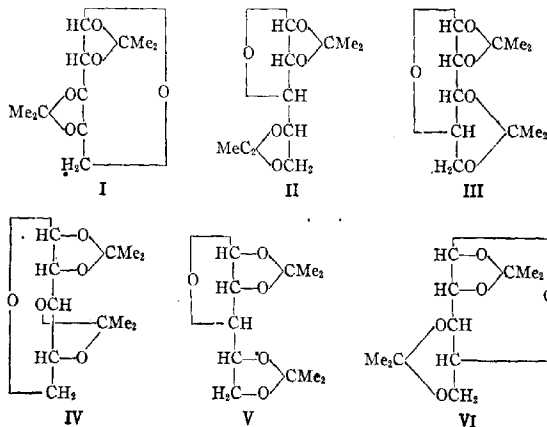
G. J. WEST

Acetonesugar. I. Rearrangements of diacetoneglucose. KARL FREUDENBERG and FRITZ BRAUNS. *Ber.* 55B, 3232-8 (1922).—Diacetonehydrazinoglucose (A) was prepd. by heating for 20 hours at $140-5^\circ$ 20 g. diacetoneoluenesulfoglucose (B) (cf. C. A. 16, 3635) with 50 g. N_2H_4 , extg. with Et_2O , washing the ext. with 50% KOH, drying over K_2CO_3 , evapg. *in vacuo* over H_2SO_4 , washing with cold Et_2O and recrystg. from Et_2O ; A is readily sol. in H_2O , MeOH, $EtOH$, Me_2CO or $CHCl_3$, m. $96-7^\circ$, reduces cold Fehling soln. and decomps. on exposure to air, $[\alpha]_D^{17} 83.4^\circ$ (H_2O); it forms a compound with acetone in soln. of the latter, giving $[\alpha]_D^{18} 163.6^\circ$; A and PhCHO in Et_2O give on partial evapg. of Et_2O and recrystn. from MeOH + H_2O by evapg. *in vacuo*, a benzal (or benzylidene) derivative (C) m. $99-100^\circ$, readily sol. in MeOH, $EtOH$, Et_2O , Me_2CO , $CHCl_3$ or PhH, slightly sol. in ligroin and insol. in H_2O , $[\alpha]_D^{18}$

144.2° ($C_2H_5Cl_4$). The mother liquors of **C** were evapd. to dryness, treated with Na_2CO_3 soln. and steam distd., giving *diacetoneglucoenose* (**D**), crystals from petr. ether, m. 51°, volatile in steam, sol. in org. solvents, slightly sol. in H_2O , $[\alpha]_{H_2O}^{17}$ 21.56° (abs. EtOH), decolorizes Br water; after hydrolysis with mineral acids it reduces Fehling soln. *Diacetonedesoxyglucose* (**E**), obtained by reduction of **D** in AcOMe with Pt and H_2 , evapg. *in vacuo* and crystg. from petr. ether, m. 80°, $[\alpha]_{H_2O}^{25}$ -3.46-34.9° (abs. EtOH), $[\alpha]_{H_2O}^{20}$ -61.9° (H_2O). Reduction of **A** in 80% EtOH with 2% Na-Hg gave diacetoneglucose (**F**) and $MeC_4H_9SO_3H$. The formulas suggested, for these compds. are based



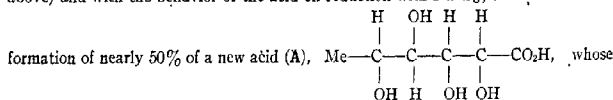
upon those given by Karrer and Herwitz (cf. *C. A.* 16, 60). II. *Diacetonexylose*. KARL FREUDENBERG and OLOF SVANBERG. *Ibid* 3239-42.—If Me_2CO reacts only with the OH groups of 2 adjacent C atoms then in arabinose the first mol. of Me_2CO is attached to C atoms 1 and 2 (cf. above for numbering) since the compd. does not reduce Fehling soln., and the second mol. of Me_2CO is attached to C atoms 3 and 4 (I) or 4 and 5 (II); the O bridging atom is therefore attached to C atoms 1 and 5 or 1 and 3. If, however, Me_2CO does not react with adjacent C atoms but forms a 6-membered ring then formula III is possible; other formulas are very improbable. The conclusion may be drawn that diacetonearabinose does not have a 1-4 O bridging and that the Me_2CO does not form rings other than 5-membered (cf. *C. A.* 16, 60). Xylose (A) has been found to react with 2 mols. Me_2CO and, therefore, the formulas IV, V and VI are possible; it is thought that glucose, which resembles A, must have a free OH on C atom 6. *Diacetonexylose* (B)



was prepd. by shaking 10 g. A and 500 cc. dry Me_2CO contg. 4.2 g. HCl for 20 hrs., adding PbCO_3 and shaking until neutral to Congo, filtering, evap. to a sirup, adding Et_2O filtering and evap. *in vacuo* below 30° ; the residue was purified by distn., $b_{\text{a.}}$ $85-7^\circ$, forming a colorless oil which is sol. in org. solvents and does not reduce Fehling soln. until after hydrolysis with HCl; a 3% aq. soln. changed in rotatory power from $[\alpha]$ 13.8° to a final value after several days of -1.3° ; a sample of B after 10 days when dissolved in H_2O gave a value of about 6° ; these optical properties are to be described later by S. The residue from the distn. when dissolved in $\text{Me}_2\text{CO} + \text{HCl}$ gave a small yield of B. B may be prepd. with lower yields by substituting $\beta\text{-C}_{10}\text{H}_7\text{SO}_3\text{H}$ for HCl.

N. A. LANGE

New (observations) in the chemistry of the sugars. IV. H. KILIANI. *Ber. 55B*, 2817-26(1922); cf. *C. A.* 16, 2679.—I. *Oxidation of sugars and poly-HO acids with HNO_3 without heating.*—This can be improved still further; the excess of HNO_3 is removed by shaking the suitably dild. soln. 5-6 times with 1.5 vols. Et_2O (the exts. are collected over 1:3 NaOH and the Et_2O can then be used again); the aq. layer, contg. the oxidation products (and nitrate esters), is allowed to stand 12-24 hrs. in a bowl and then coned. *in vacuo* over H_2SO_4 , owing to the lability of the ketonic acids present, the soln. generally quickly becomes yellow and red, but after a certain concn. has been reached it again gradually pales out and gas is evolved, the nitrate esters gradually hydrolyzing to free HNO_3 which produces a renewed oxidation. An illustration of the advantages of this modification of the method is the fact that it makes it possible to detect *l*-trihydroxyglutaric acid as a by-product in the "last mother liquors" in the prepn. of ketorhamnolactone (*C. A.* 16, 2120); again, oxidation of α -glucoheptonic acid with HNO_3 of d. 1.35 and treatment with Et_2O as above gives 22-5% of inactive pentahydroxypimelic monolactone, m. 150° (previously given as 143°); *quinine salt*, $\text{R}_4\text{C}_4\text{H}_{10}\text{O}_4 \cdot 4\text{H}_2\text{O}$ ($\text{R} =$ the base); *brucine salt*, short stout microcolumns with $6\text{H}_2\text{O}$ from 85% alc. II. *d*-Glucose and HNO_3 .—The strongly reducing acid obtained from *d*-glucose (and *d*-gluconic acid) with HNO_3 has now been identified with Boutroux and Bertrand's "hydroxygluconic acid"; the crude Ca salt can be obtained in quite pure condition and in not too small yield (15-6 g. from 100 g. glucose) by pptn. with CaCl_2 in a soln. strongly acid with AcOH (instead of a nearly neutralized soln.). It would probably be better now to designate the acid as *5-keto-d*-gluconic acid; it slowly forms a *semicarbaside salt semicarbazone*, $\text{C}_6\text{H}_{18}\text{O}_8\text{N}_4$, becomes discolored 170° , softens 200° . III. *Constitution of ketorhammonic acid.*—The lactone of this acid at once gives CHI_3 in abundance when treated with I-KI and KOH, while under the same conditions rhamnose solns. remain clear. It is concluded that in the ketone the CO is attached directly to the Me group, *i. e.*, occupies position 5 instead of 2 as believed previously. This view is in harmony with the formation of *l*-trihydroxyglutaric acid as a by-product in the prepn. of the lactone (see above) and with the behavior of the acid on reduction with Na-Hg; this results in the

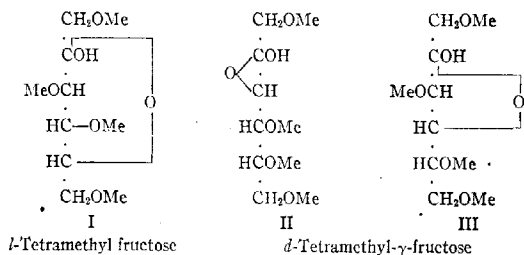


lactone, mostly columns from 85% alc., long stout tables from H_2O , m. 152° , $[\alpha]_D -84.9^\circ$ immediately after soln., -50° after 16 hrs. The K, Na and Ba salts are amorphous; *brucine salt*, stout tables with $7\text{H}_2\text{O}$, softens 70° , m. 132° ; *phenylhydrazide*, stout needles, m. 152° ; *hydrazide*, needles, m. $155-6^\circ$, $[\alpha]_D 15.2^\circ$. K. had intended to name A *5-epi-l*-rhammonic acid but Freudenberg suggests that the names of still unknown methylpentoses be referred back to the hexoses with corresponding configurations and be given the ending "eose" (as in rhodose) and that A, therefore, as a reduction product from ketorhamnolactone, be called *l*-guleonic acid. IV. *Levulosecarboxylic acid.*—The phenyl-

hydrazide can be obtained directly from the sirupy crude acid if the latter, moderately dild. with 85% alc., is allowed to stand a long time with PhNHNH_2 in sealed tubes; it seps. from H_2O in stout columns, m. 187° , $[\alpha]_D -29.5^\circ$ (H_2O , c 4.798), gives the Bülow Fe reaction normally. This l -rotation is directly contrary to Nef's assumption as to the position of the α -HO group (C. A. 5, 85); moreover, K.'s recent observations make it highly improbable that "HCN is taken up entirely asymmetrically by levulose."

C. A. R.

1,3,4,6-Tetramethylfructose. J. C. IRVINE AND JOCELYN PATTERSON. *J. Chem. Soc.* 121, 2696-703(1922).—Because of the discovery of γ -fructose in the hydrolysis products of sucrose and inulin, it is desirable to extend our knowledge of the normal isomer. For its prepn. tetraacetylfructose was chosen as the starting material, it in turn being prepd. from β -Me fructoside. The temp. should be kept low during the 1st 15 mins. of the reaction. This product is then transformed into the β -Me deriv., the Ac groups are removed by NH_3 in MeOH, the β -Me fructoside is changed into the tetra-Me deriv., and this finally hydrolyzed in the usual manner. Good yields were obtained in each operation. After 6 crysts. the pure α -1,3,4,6-tetramethylfructose (A) was obtained as square plates, m. $98-9^\circ$. It showed the following mutarotations: H_2O (c 1.802) -124.3° to -123.2° in 2 hrs.; EtOH (c 2.102) -91° to -87.7° in 3 days; C_6H_5 (c 1.507) -116.6° to -84.7° in 7 days (cf. Purdie and Paul, C. A. 1, 1542, 1696). A soln. in aq. 0.1 N NaOH showed an initial optical exaltation which diminished irregularly until the darkening of these solns. prevented further observations. The 2 sugars condense with MeOH at widely different speeds, the γ -deriv. requiring only 24 hrs. for complete condensation while the l -form required about 70 days. The same difference is seen in their rates of hydrolysis. A was not appreciably attacked by neutral KMnO_4 after 20 days. The action of alk. KMnO_4 appears to involve enolization and rupture of the ketose mol. between the 2nd and 3rd C atoms of the chain. Dil. HNO_3 is a more satisfactory oxidizing agent, the main product being a diethyl dimethoxyhydroxyglutarate, b_{0.25} 130° , m. $86-7^\circ$, n_D 1.4643. The various possible formulas for the 2 isomers are discussed but no decision is reached as to whether II or III best explains the reactions of the γ -fructose.



C. J. WEST

Glucosidotrimethylammonium salts. P. KARRER AND J. TER KUILE. *Helvetica Chim. Acta* 5, 870-6(1922); cf. C. A. 16, 65.— $\text{C}_6\text{H}_7\text{O}_5\text{Ac}_3\text{NMe}_3\text{Br}$ forms transparent rhomboids, $a : b : c :: 0.4520 : 1 : 0.3443$; $m(110)$, $b(011)$, $b(010)$. Tetraacetyl-*d*-glucosido-*l*-trimethylammonium chloride, from the bromide and AgCl, hygroscopic crystals, m. 173° . Perchlorate, broad needles, m. 190° . Picrate, fine yellow needles, m. 133° . Chloroplatinate, fine orange needles, m. $209-10^\circ$ (decompn.). Chloroaurate, yellow needles, decompd. by heat. Hydrolysis with mineral acids splits off the Ac groups. *d*-Glucosido-*l*-trimethylammonium bromide, compact hygroscopic crystals, m. $161-2^\circ$. Chloride, very hygroscopic. Iodide, m. $162-3^\circ$. Chloroplatinate, orange-brown crystals.

Chloroaurate.—*Picrate*, yellow needles, m. 141° . Treated with $\text{Ba}(\text{OH})_2$ the bromide yields levoglucosan.

C. J. WEST

Oxidation of sucrose by nitric acid. F. D. CHATTAWAY AND H. J. HARRIS. *J. Chem. Soc.* 121, 2703-9(1922).—Although the oxidation of sucrose by HNO_3 was first studied 150 yrs. ago, little close attention has been paid to the subject and $(\text{CO}_2\text{H})_2$ has been generally regarded as the sole end-product. It is now shown that *mesoxalic acid* is formed in considerable quantity. *700 g. HNO_3 (d. 1.41) are added to 50 g. sucrose in a 1500-cc. flask and the mixt. is heated to $72-5^{\circ}$. The heat is removed and, after the violent action has subsided—about 25 min.—the liquid is poured into an evap. dish and boiled rapidly until, when cooled to 74° , it occupies a vol. of 112 cc. It is then transferred to a flask, cooled to -5° , the $(\text{CO}_2\text{H})_2$ which seps. filtered off and then 5 g. Na_2CO_3 (anhydrous) added in 3 portions. After cooling to -5° , the NaNO_3 is filtered off, an additional 12 g. Na_2CO_3 added and then satd. aq. Na_2CO_3 until the liquid is distinctly alk. On standing 24 hrs. 5-6 g. $(\text{HO})_2\text{C}(\text{CO}_2\text{Na})_2$ sep. The other common carbohydrates, dextrose, levulose, lactose, maltose and starch also yield this acid when violently oxidized with HNO_3 . The following hydrazones of mesoxalic acid are described (the 1st figure for the m. p. is that at which the compd. melts when held at that temp. for 1 min.): *p*-Chlorophenylhydrazone, bright yellow, elongated prisms, m. 186.5° , $192-3^{\circ}$; *o*-derivative, bright yellow, elongated prisms, m. 175° , 182° ; *2,4*-dichlorophenylhydrazone, bright yellow prisms, m. 182.5° , 188° ; *p*-bromophenylhydrazone, bright yellow, long, slender prisms, decomp. without m.; *2,4*-dibromophenylhydrazone, bright yellow, very much elongated prisms, decomp. about 205° ; *p*-tolylhydrazone, pale yellow, short, flattened prisms, m. 170.5° , 178° ; *o*-derivative, bright yellow slender prisms, m. 163.5° , $171-2^{\circ}$.

C. J. WEST

Constitution of glucosan. MARC CRAMER AND E. H. COX. *Helvetica Chim.*

Acta 5, 884-7(1922).—The constitution of glucosan, $\begin{array}{c} \text{CH}-\text{CH}-\text{CH}(\text{OH})-\text{CHCH}_2\text{OH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array}$

$(\text{OH})\text{CH}_2\text{OH}$ (A) (Pictet and Castan, *C. A.* 14, 3226), questioned by various authors, has been confirmed. Tribenzoylglucosan does not give an osazone; but that is because it is not hydrated except under conditions which split off BzOH . Trimethylglucosan (B), b.p. $210-2^{\circ}$, was obtained in rather poor yield by methylating A at $35-40^{\circ}$ with alk. Me_2SO_4 . B gives a reducing sugar on boiling with H_2O , showing easy hydration; its osazone (C), yellow crystals, m. $113-4^{\circ}$ (decompn.), and the formation of C proves the structure A. When A was heated some hrs. with MeI at $125-30^{\circ}$, an addn. product was formed. This, reduced with Na-Hg in cold soln. kept just alk., gave 2-deoxymethylglucoside (D) as a thick sirup. D was thoroughly identified through its tri-Ac deriv., previously known. The structure of A is thus doubly confirmed. B. H. N.

Polysaccharides. XVI. P. KARRER (WITH W. FLORONI). *Ber.* 55B, 2854-63 (1922); cf. *C. A.* 16, 1747.—By means of a very accurate combustion bomb (to be described in *Helvetica Chim. Acta* by Schläpfer and Floroni) the heats of combustion (h. c.) of the amyloses and other carbohydrates have been detd. anew with an accuracy of 0.1-0.2%. Below are the values (in cal.) for 1 g. dry substance: diamylose 4285, α -tetraamylose 4196, α -octaamylose 4620, β -hexaamylose 4166, levoglucosan 4181, "tri-amylose" (identical with β -hexaamylose) 4165.2. The conclusions drawn from the earlier measurements require no modification. To obtain further data on the question whether for any sugar of the general formula $(\text{C}_6\text{H}_{12}\text{O}_6)_n - (n-1)\text{H}_2\text{O}$ the h. c. can be approx. calcd. beforehand, the measurements have been extended to other substances. Cellobiose, crystd. from H_2O until ash-free and dried *in vacuo* at 110° (it then contains 0.5, not 0.25 mol. H_2O), gave a h. c. (for the anhyd. sugar) of 3944 cal.; for cane sugar, milk sugar and maltose the values are 3945, 3953 and 3949, resp., i. e., the same within

the limits of error of the method. Likewise, the h. c. of maltose and cellobiose octaacetates are 4468 and 4471 cal., resp. For the tetrasaccharide stachyose the h. c. is 3808 cal. for the sugar with 2.5 H₂O or 4065 cal. for the anhyd. sugar (calcd. theoretically, 4058). For starch and cellulose hexaacetates and inulin triacetate the h. c. are 4499, 4496 and 4522 cal., resp.; the corresponding mol. h. c. are 1296.5, 1284.8, 1302.3 kg.-cal. while the values calcd. from the h. c. of 1 g. starch, cellulose and inulin (4182, 4185, 4190 cal.) and the mol. h. c. of AcOH (209.5 kg.-cal.) on the assumption that the heat of formation in the reaction $C_6H_{10}O_5 + 3AcOH = C_6H_7O_5Ac_3 + 3H_2O$ is very small are 1306.0, 1306.5 and 1307.3; these results indicate that in the acetylation there is no material change in the degree of polymerization of these carbohydrates. A detailed answer is made to the criticism of Pringsheim (*C. A.* 16, 3878). C. A. R.

Polysaccharides. XVII. Chitin. P. KARRER AND A. P. SMIRNOFF. *Helvetica Chim. Acta* 5, 832-52(1922); cf. *C. A.* 16, 1747.—The distn. of 300 g. chitin (10-g. lots with 200 g. Zn dust for each) gave 37 g. crude oil, consisting of C₈H₉N-bases, sepd. by extn. of the Et₂O soln. with 5% H₂SO₄ (probably α -picoline) and *chitopyrrole*, proved by synthesis from 2-methylpyrrole, C₆H₁₃I and K to be *2-methyl-1-hexylpyrrole* (A), b. 200-10°, turns brown upon standing a short time in the air, gives an intense red pine stick reaction but does not give a cryst. deriv. Oxidation of A with CrO₃ in AcOH at room temp. for 24 hrs. or with NaNO₂ in H₂SO₄ for 0.5 hr. gave maleic acid and C₆H₁₃NH₂. For comparison *2,5-dimethyl-1-amylypyrrole*, b. 225-7°, was prepd. from [MeC(OH):CH]₂ and C₆H₁₁NH₂ by heating 2 hrs. at 140°. Upon oxidation this gave (HO₂CCH)₂ and C₆H₁₁NH₂. Distn. of glucosamine or its HCl salt with Zn dust gave much NH₃ and only traces of C₆H₅N bases. These facts indicate that in chitin 1 glucosamine mol. is bound to a 2nd through the NH₂ group. The small yield of pyrrole deriv. would indicate, however, that there are other forms of linkages in the chitin mol.

C. J. WEST

Cork substance. P. KARRER, J. PEYER AND ZORKA ZEGA. *Helvetica Chim. Acta* 5, 853-63(1922).—Many earlier workers have stated that cork substance contained cellulose but the exptl. evidence thus far presented is not convincing. Cork was extd. with Et₂O, CHCl₃ and EtOH to remove cerin, etc., then sapond. with 3% EtOH-KOH to remove fatty acids and finally heated with 5% NaHSO₃ to remove lignin. 1250 g. extd. cork gave 100 g. cork residue (A). 35 g. A, warmed 0.25 hr. with 400 g. Ac₂O and 24 g. ZnCl₂, gave 1.4 g. of *cellulose triacetate* (B), $[\alpha]_D^{18} -21.2^\circ$, which gave 72% glucose upon hydrolysis. 1.4 g. A gave only 0.05 g. *cellobiose octaacetate* when treated with Ac₂O and H₂SO₄, and an equally poor yield of *acetobromocellobiose* when treated with AcBr. These yields are due in part to impurities. About the same yield of B is obtained when the unsapond. cork is used. While these facts prove the presence of cellulose in cork substance, they also indicate, because of the small yields, the presence of other carbohydrates. *Levogluconan tripalmitate* was prepd. by the action of C₁₈H₃₇COCl upon levogluconan in CHCl₃ contg. C₆H₇N, m. 68.5°, $[\alpha]_D^{18} -21.08^\circ$; the *tristearate* m. 73.4° and has $[\alpha]_D^{18} -18.40^\circ$. *Cellulose hexapalmitate*, m. about 78°, $[\alpha]_D^{22} -3^\circ$, was obtained when cellulose pptd. from Schweitzer's reagent by acid was heated with C₁₈H₃₇COCl in C₆H₇N for 4 hrs. at 120°.

C. J. WEST

Additive properties between cresols and alcohols, etc. E. BERL AND W. SCHWEBEL. *Z. angew. Chem.* 35, 398(1922).—Polemic. Cf. *C. A.* 16, 3881. H. G.

Application of the tension theory to the ring systems of cholesterol. A. WINDAUS AND W. HÜCKEL. *Nachr. kgl. Ges. Wiss. Göttingen, Math-physik. Klasse* 1921, 162-83.—Theoretical discussion. C. J. WEST

Saponins. III. Saponins from the leaves of *Aralia montana* Bl. (Galacturonoid saponins, their magnesium and calcium salts.) A. W. VAN DER HAAR. *Ber.* 55, 3041-69 (1922).—The main results are essentially the following. The alc. of the leaf wax is my-

ricyl alc. The powdered leaves and stems contain together about 1.6% saponin, representing at least 3 different groups. It occurs both free and combined in the form of the Mg and Ca salts which are not pptd. by normal, but are pptd. by basic Pb acetate. In order to isolate the saponins, resort is had to Boersma's MeOH method followed by extrn. with 45% EtOH, the latter operation yielding the salts. These compds. are toxic to fishes and show hemolytic action, the Mg salt being 3 times as toxic as the free saponin. *Aralia* saponins yield the violet H_2SO_4 test like the ordinary saponins. They are hydrolyzed with difficulty into *l*-arabinose, a methylpentose, *d*-glucose, *d*-galactose, *d*-galacturonic acid, and sapogenins. Each saccharide was quant. detd. No other saccharides and acids were detected. A colorless chem. pure cryst. sapogenin (*araligenin*) m. 275° was isolated from the sapogenin mixt. The pure substance sublimes and crystals from EtOH with EtOH of crystn. With varying amts. of this EtOH of crystn., the m. p. varies from 273° to 311° . Dried at 150° , araligenin has the compn. $C_{25}H_{40}(OH)CO_2H$, shows $\alpha_D^{20} 71^\circ$ (in $C_6H_5N + EtOH$), gives the Liebermann cholesterol reaction (violet, then blue and finally green). A cryst. *polassium salt*, *methyl ester* m. 180° and *monoacetyl methyl ester* m. $217-8^\circ$ were prepd. Araligenin contains an OH, which, on account of steric interference of the free CO_2H , cannot be acetylated in the usual way. The latter group must first be esterified, whereupon acetylation is easily effected. On distn. with Zn dust in an atm. of H_2 , araligenin is split into H_2O , CO_2 and terpene hydrocarbons, separable into a light volatile (with steam) portion, yielding the violet $AcOH-H_2SO_4$ reaction, and a non-volatile portion yielding first a blue and later green $AcOH-H_2SO_4$ test. The volatile portion is an oil with a terpene-like odor; it has the compn. $(C_8H_8)_n$. The decompn. above indicated may be represented by the equation: $C_{25}H_{40}(OH)CO_2H = (C_8H_8)_3 + CO_2 + H_2O$. W. O. E.

Vinylcyclopropane, some derivatives of methylcyclopropylcarbinol and the isomerization of the cyclopropane ring. N. J. DEMJANOW AND MARIE DOJARENKO. *Ber.* 55B, 2718-27 (1922).—Since Gustavson's "vinyltrimethylene," obtained from pentaerythritol tetrabromide, has been shown by other investigators really to be 1-methylenecyclobutane (A) (cf. also following abstr.), usually accompanied by small amts. of the isomeric methylcyclobutene (B), it became of interest and importance to prep. in another way A and the true vinyltrimethylene or vinylcyclopropane (C). After vainly trying various methods usually employed for prep. unsatd. hydrocarbons, Hofmann's finally led to the desired result. It proved especially satisfactory, as regards the yield, for the prepn. of C, as the decompn. in this case proceeded chiefly according to the scheme $RCHMeNMe_3OH$ (D) \longrightarrow $RCH:CH_2$ (C) + $NMe_3 + H_2O$ ($R = CH_2CH_2CH-$)

and not in the other possible way, D \longrightarrow $RCHMeNMe_3$ (E) + MeOH, while exactly the opposite is true in the case of A (following abstr.). Attempts to use RCHMeOH as the starting point failed, chiefly because the ring was ruptured or the hydrocarbon was formed only in minimal amt., as was the case in the action of $(CO_2H)_2$ on E; at the same time isomerization occurred and the hydrocarbon consisted chiefly of piperylene (F). $RCHMe: NOH$ (99 g.) yielded, together with 14 g. unchanged oxime, 69 g. $RCHMeNH_2 \cdot HCl$, 67 g. of which with MeI and KOH in MeOH gave 140 g. trimethyl[α -cyclopropylethyl]ammonium iodide, long, almost colorless prisms from alc.; 123 g. of this, converted in 20-5-g. portions with Ag_2O into D and distd., gave 22 g. C and such a small amt. of dimethyl[α -cyclopropylethyl]amine (E) that it could not be isolated in the free form; its picrate, long yellow needles from alc., m. $187-8^\circ$; chloroaurate, slender yellow rectangular leaflets from H_2O . C, mobile liquid of penetrating leek-like odor, $b_{78} 40-0.2^\circ$, d 0.741, 0.731, 0.726, 0.723 at 0° , 10° , 15° , 18° , resp., $n_D^{20} 1.4205$ and 1.4172 at 10° and 15° . Dibromide, obtained almost quant. with Br in ice-salt, $b_{21-2} 86-8^\circ$, d 1.842, 1.825, 1.818 at 0° , 10° and 15° , $n_D^{19} 1.54447$; further action of

with PbO_2 in H_2O gives cyclopentanone (**B**) in good yield (60%), together with traces of *cyclobutanedialdehyde* (**C**), which explains the formation of large amts. of **B** observed by Gustavson when he heated the dibromide of his "vinyltrimethylene" with PbO_2 and H_2O in sealed tubes at $135\text{--}40^\circ$ (*J. prakt. Chem.* **56**, 93 (1897)), and it has been found in D's lab. that this last transformation can be effected by boiling several hrs. on the H_2O bath and even on long standing (several months) at room temp. if the soln. is shaken frequently. In the formation of **B** from the dibromide a Br compd. analogous to **A** is probably an intermediate product. An intermediate cyclopentanone deriv. is also probably formed in the oxidation of **A** with HNO_3 , which yields far more glutaric acid (2.8 g., together with 0.4 g. succinic acid, from 5 g. **A**) than methylenecyclobutane (**D**) itself or any other of its derivs. **A**, obtained in 50% yield from **D** and the calcd. amt. of HOCl (from AcOH and CaOCl_2), b. 64.5° , 75° , 83° , 158° under 20, 33, 47 and 747 mm., resp., $d_4^{16.57}$, 1.502, 1.448 at 0° , 15° and 20° , $n_D^{16.57}$ 1.657; phenylurethane, needles from

CHCl_3 -petr. ether, m. 112.5–3.0°. The oxide $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)\text{O}$, obtained in

51% yield from **A** and hot concd. aq. KOH, b_{744} 89–92°, d_4 0.9284, 0.9133 at 0° and 15°, n_D^{15} 1.4230, is isomerized by dropping into anhyd. ZnCl_2 into **C**, which forms a solid NaHSO_4 compd., colors fuchsin- SO_2 intensely red-violet, gives with Ag_2O a silver salt, $\text{C}_6\text{H}_7\text{O}_2\text{Ag}$, sepg. from H_2O in crystals. In the prepn. of **A** there is also formed the dichloride of **D**, b_{88} 67–9°, d_4 1.1928, 1.1772 at 0° and 15°, n_D^{15} 1.4756. C. A. R.

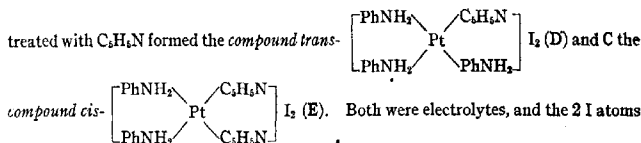
Preparation of cyclobutanone by pyrochemical decomposition of 1-hydroxycyclobutane-1-carboxylic acid. N. J. DEMJANOW AND MARIE DOJARENKO. *Ber.* 55B, 2737–42 (1922).—1-Bromocyclobutanecarboxylic acid, obtained in 71 g. yield from 48 g. $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ by Perkin's method (*J. Chem. Soc.* 61, 42 (1892)), b_{40-45} 145–55°; refluxed 5 hrs. in 2 parts H_2O with 0.5 mol. K_2CO_3 it gives 94% of the HO acid (**A**) and its anhydrides; 10 g. of this product, decompd. at 280–300°, evolves 700–800 cc. gases (chiefly CO , with about 10% CO_2) and yields 15% cyclobutanone (**B**), $b.$ 92–100°; semicarbazone feathery aggregates with pearly luster from alc., m. 212° (decompn.); dibenzal derivative, from **D** in 60% alc. with the calcd. amt. of BzH and alc. KOH, leaflets from CHCl_3 , m. 170–1°, is turned orange-red by a drop of concd. H_2SO_4 . *Anhydrides of A:* (1), $\text{C}_{10}\text{H}_{12}\text{O}_4$, remains as a cryst. residue when **A** is distd. under 8–10 mm. or as an insol. residue when the crude **A** is treated with H_2O , m. 65°, mol. wt. in boiling Et_2O 215–6, in freezing C_6H_6 368–89; (2) along with the above, there remain, on distn. of **A**, non-cryst. anhydrides insol. in all solvents, decomp. on heating into CO_2 and **B**, are unchanged by heating with an excess of H_2O up to 120°; at 150–60° the tube exploded but the solid, a light porous fibrous mass entirely different from the original product, was collected; its compn., $(\text{C}_{10}\text{H}_{12}\text{O}_4)_x$, corresponded to $4\text{C}_4\text{H}_8\text{O}_3 \cdot 3\text{H}_2\text{O}$. C. A. R.

Equilibrium in the system *m*-dinitrobenzene-urethan. N. A. PUSHIN AND ALEXANDRA FROLITOVA. *J. Chem. Soc.* 121, 2822–3 (1922).—The eutectic point of the system $m\text{-C}_6\text{H}_3(\text{NO}_2)_2$ -urethan corresponds to a concn. of 91 mol. % urethan and lies at 42.3°. The solid phase of the system must be, at every concn., a mech. mixt.

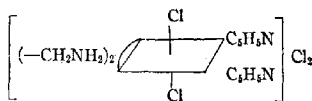
C. J. WEST

Occurrence of phenylcarbamylamine and nitrobenzene in aqueous aniline solutions. H. KUNZ-KRAUSE AND P. MANICKE. *Ber. pharm. Ges.* 32, 232–6 (1922).—The observed occurrence of a PhNC -like odor in certain mixts. of H_2O and supposedly pure PhNH_2 when exposed to sunlight is due to the presence of some as yet unidentified impurity, since absolutely pure PhNH_2 - H_2O mixts. yield no such odor after several months' exposure, although PhNH_2 in contact with H_2O gradually becomes brown to red, with deposition of resinous or tarry products on exposure to strong light, such products dissolving in concd. H_2SO_4 with the formation of a Bordeaux-red color. The formation of PhNO_2 in PhNH_2 - H_2O mixts., even in the case of pure PhNH_2 , on protracted exposure to strong light, is due to oxidizing influences, similar to those obtained with CaOCl_2 or KMnO_4 , leading to the rise of intermediate products which are thereupon oxidized to PhNO_2 . W. O. E.

Complex compounds with the coordination number five. A. SCHLEICHER, H. HENKEL AND L. SPIES. *J. prakt. Chem.* 105, 31–8 (1922).—Analogous to the formation of $[\text{Pt}(\text{NH}_3)_2(\text{PhNH}_2)_2]\text{SO}_4$ from *cis*- $[\text{Pt}(\text{NH}_3)_2\text{SO}_4]$ and PhNH_2 (**A**), *trans*- $[\text{Pt}(\text{NH}_3)_2\text{I}_2]$ was treated with **A**. But a very small yield of the compound *trans*- $[\text{Pt}(\text{NH}_3)_2(\text{PhNH}_2)_2]\text{I}_2$ and a good yield of the compound *trans*- $[\text{Pt}(\text{PhNH}_2)_2\text{I}_2]$ (**B**) of a bronze color, and an unidentified violet amorphous powder were obtained. Direct treatment of PtI_2 with **A** in an attempt to form **B** gave the compound *cis*- $[\text{Pt}(\text{PhNH}_2)_2\text{I}_2]$ (**C**), bright yellow crystals. By treating *cis*- $[\text{Pt}(\text{NH}_3)_2\text{I}_2]$ with **A**, the same compd. was formed. Treatment of K_2PtCl_4 with NH_3 (cf. Ramberg, *C. A.* 8, 31) and the resulting *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ successively with AgNO_3 and KI gave the compound *cis*- $[\text{Pt}(\text{NH}_3)_2\text{I}_2]$. **B**



reacted in the cold with $AgNO_3$. Treated with concd. HCl , D formed a mixt. of B and the compound *trans*- $[Pt(C_6H_5N)_2I_2]$ of a white color, and E the compound *trans*- $[Pt(PhNH_2)(C_6H_5N)I_2]$. B was sol., C almost insol. in aq. $(-CH_2NH_2)_2$ (F). Addn. of $EtOH$ to the C-F mixt. gave a brown oil which after evapn. *in vacuo* and treatment with H_2O crystd. to the compound $[Pt((-CH_2NH_2)_2)I_2]$ (G), white crystals. No *cis*- $[Pt(PhNH_2)_2(-CH_2NH_2)_2]I_2$ was formed. G was also obtained from a B-F mixt. Aq. G gave with dil. H_2SO_4 a yellow color with pptn. of PtI_2 . By spontaneous evapn. of the filtrate, a yellow compd. was obtained on which data are to be published forthwith. No addn. product of NH_3 or of C_6H_5N could be formed with diethylenediamine chloroplatinate (H). The unidentified compd. of Kurnakov (cf. *Z. anorg. Chem.* 17, 226 (1898)) from H and Cl could not be obtained, but the valence of Pt increased and $Pt[(-CH_2NH_2)_2]_2Cl_4$ in 3 modifications, according to H_2O content, was obtained. By pptn. with abs. $EtOH$, the compound $Pt[(-CH_2NH_2)_2]_2Cl_4 \cdot 2H_2O$ was obtained, white crystals. By letting the original soln. stand over P_2O_5 and subsequent fractional crystn. the compound $Pt[(-CH_2NH_2)_2]_2Cl_4 \cdot 1H_2O$, interpenetrated yellowish crystals, and the compound $Pt[(-CH_2NH_2)_2]_2Cl_4 \cdot 3H_2O$ were obtained. Treatment of these hydrates with K_2PtCl_6 gave the compound $[Pt((-CH_2NH_2)_2)_2Cl_2](PtCl_6)$, brownish white, insol. in H_2O . Aq. H and alc. Br formed the compound $[Pt((-CH_2NH_2)_2)_2Br_2]Cl_2 \cdot 2H_2O$, yellow, turning green in the air. $AgNO_3$ formed a white, cheesy ppt. and K_2PtCl_6 a yellow insol. salt. Both Cl atoms in these compds. are assumed to be in the *trans*-position to the plane of both F mols. Chlorination of $Pt[(-CH_2NH_2)_2]_2Cl_2$ gave the compound $Pt[(-CH_2NH_2)_2]_2Cl_4$ (I), yellow crystals. Boiling I with F formed not the expected isomer, but triethylenediamine chloroplatinate (cf. *Vierteljahrsschr. Naturforsch. Ges. Zürich* 62, 553 (1917)). I and cold C_6H_5N formed the compound $Pt[(-CH_2NH_2)_2(C_6H_5N)_2]Cl_4$ (J). Replacement of the C_6H_5N by F gave on drying the same compd. obtained by chlorination of H. To J is assigned the structure:



C. C. DAVIS

Esters of the hydroxyalkylarylamines. I. Acid sulfuric esters of the simple monohydroxyethylarylamines. K. H. SAUNDERS. *J. Chem. Soc.* 121, 2667-75 (1922).—The alkylsulfuric acid group attached to N is termed the "sulfato" group, and the process of esterification as "sulfation." These esters may be prepd. in 3 ways: By soln. in concd. H_2SO_4 in such excess that esterification proceeds virtually to completion. This process is beset with the same difficulties found in the attempt to isolate H_2SO_4 itself in high yield and purity. A 2nd method consists in acting on arylamines with $ClCH_2CH_2OSO_3H$, which has the disadvantage that the latter must be prepd. from anhydrous HOC_2H_4Cl and the yields are not always good. The 3rd method consists in esterifying with $ClSO_3H$ which may be used alone or in an indifferent solvent. In this reaction the neutral ester is also obtained in varying amts. Chemically these sulfato compds. show reactions characteristic of the units of their structure—arylamine and alkyl sulfate. *N*-Phenyl- β -aminoethyl hydrogen sulfate (sulfatoethyl aniline), prepd. by each of the above

3 methods, rectangular laminas, m. 206°; it decolorizes Br-H₂O but does not react with CuSO₄. It is sol. to the extent of 5% in boiling and 1-2% in cold EtOH. It is very slowly hydrolyzed by H₂O below its b. p.; HCl accelerates the hydrolysis, which has a value of *k* for a monomol. reaction. Practically no hydrolysis was found after heating with 0.2 or 0.8 *N* NaOH at 70° for 5 hrs.; heated with 3 mols. NaOH for 1 hr., 20.4% of the salt had hydrolyzed. *Sodium salt*, with 1 H₂O, leaflets, sol. to the extent of 60 g. per 100 cc. of soln. at 15°; *potassium salt*, leaflets; 23 parts dissolve in 100 cc. H₂O at 15°; *ammonium salt*, leaflets, m. 132°, of which 70 g. dissolve in 100 cc. H₂O at 15°. *N-o-Tolyl-β-aminoethyl hydrogen sulfate*, rectangular laminas, m. 203°. *N-Phenyl-N-ethyl-β-aminoethyl hydrogen sulfate*, hard granules, m. 208°. Treated in *N* NaOH with solid NaNO₂ after which concd. HCl was slowly added, this gave the *p*-nitroso derivative, dark green dust, decomp. 170-80°, readily reduced in alk. soln. *N-Phenyl-N-methyl-β-aminoethyl hydrogen sulfate*, m. 193°. *Sodium N-phenyl-N-benzyl-β-aminoethyl sulfate*, shining crystals with 2H₂O, which it loses at 100° and then m. to a waxy mass; the free acid could not be obtained cryst. *N-m-Nitrophenyl-β-aminoethyl hydrogen sulfate*, stout pale cream needles, m. 203° (decompn.). The alk. soln. is a deep orange. *m-Nitroaniline salt*, large pale yellow laminas, m. 206°. *N-p-Chlorophenyl-β-aminoethyl hydrogen sulfate*, needles, m. 217° (decompn.). *N-α-Naphthyl derivative*, m. 234° (decompn.). The coupling with diazo salts in the *p*-position to the sulfato group will be described in a later article. See also Brit. patent 181,750 of 1922.

C. J. WEST

Action of bisulfite on nitroanilines. HUGO WEIL AND PAUL WASSERMANN. *Ber.* 55B, 2533-42(1922); cf. *C. A.* 16, 3075.—It has been found that NO₂ derivs. of C₆H₅, its homologs, their halogen substitution products, nitrophenol ethers and *p*-O₂NC₆H₄CO₂H are reduced by NaHSO₃ to sulfaminic acids, while nitrophenols form easily sol. substances which have the property characteristic of sulfaminic acids of splitting off H₂SO₄ on boiling with mineral acids but at the same time change into aminophenolsulfonic acids. To det., if possible, any general relationship which might exist between the nature of a 2nd substituent, other than the NO₂ group, on the C₆H₅ nucleus and the character of the product obtained by reduction with NaHSO₃, a study has been made of the nitroanilines and some of their products. *p*-O₂NC₆H₄NHAc, boiled with 5 mols. NaHSO₃ or 3 mols. NaHSO₃ + 1 mol. Na₂SO₃, gives quant. *sodium p*-acetylaminophenylsulfaminic acid (A); the formation of compds. which, after boiling with mineral acids, appear as sulfonic acids, is in this case entirely subordinated; A on boiling with dil. mineral acids loses the SO₃H group, forming *p*-AcNHC₆H₄NH₂, but with boiling alkalis it loses only the Ac group, giving *p*-aminophenylsulfaminic acid (B) which shows the normal reactions of an NH₂ compd.; boiled with 2,4-(O₂N)₂C₆H₃Cl in alc. in the presence of a weak alkali it yields a beautifully crystd. substitution product (C) and, on cautious diazotization and coupling with β-C₁₀H₇OH, an azo dye (D) which, owing to the presence of the NHSO₂H group, is sol. in Na₂CO₃ and reprecipitated by dil. acids, but on boiling with dil. mineral acids it loses this property owing to the splitting off of the SO₃H group. *p*-Nitroacetotoluide and *p*-nitroacetylanisidine behave like O₂NC₆H₄NHAc, except that the products are more sol. and hence more difficult to isolate. The Bz also behaves like the Ac derivs., but the reaction requires considerably more time and the products are difficultly sol. Benzylated nitroanilines are not attacked in the slightest degree by NaHSO₃ even on long boiling. *p*-O₂NC₆H₄NMe₂ slowly dissolves in boiling NaHSO₃ and sulfaminic acid can be detected in the soln. but the products are extraordinarily sol. and have thus far not been isolated. The same is true of *p*-O₂NC₆H₄NH₂; if, however, the soln. of the product is concd. until most of the Na₂SO₄ has sep'd. and is cautiously treated in the cold with dil. HCl it solidifies to a magma of needles, the compn. of which, after repeated pptn. from H₂O with HCl, indicates that it is the *monosodium salt* (E) of a sulfaminic sulfonic acid, 1,2,-

4- or 1,3,4- $C_6H_3(NH_2)(SO_3H)NHSO_3H$; on boiling with HCl , it loses only one SO_3H group and yields $p\text{-}H_2NC_6H_4NHSO_3H$. The NH_2 group in **E** cannot be substituted by means of $BzCl$ or boiling $(O_2N)_2C_6H_3Cl$, nor is it diazotized by HNO_2 which reacts first with the $NHSO_3H$ group, with elimination of H_2SO_4 . $o\text{-}O_2NC_6H_4NH_2$, unlike the p -compd., gives with $NaHSO_3$ sodium *o*-anilinosulfamate (**F**). The products obtained from $m\text{-}O_2NC_6H_4NH_2$ could not be isolated on account of their soly. but can be diazotized in soln. and coupled with $\beta\text{-}C_{10}H_7OH$; the resulting azo dye has acid properties which it retains after boiling with mineral acids, although H_2SO_4 is split off in this last operation, whence it may be concluded that the m -like the $p\text{-}O_2NC_6H_4NH_2$ yields a sulfosulfaminic acid. $m\text{-}C_6H_4(NO_2)_2$ yields the sodium salts of both *m*-nitrophenylsulfaminic (**G**) and phenylene-*m*-disulfaminic acid (**H**); at low temps. and with $NaHSO_3$ without any Na_2SO_3 **G** is the chief product but on boiling and addn. of 1 mol. Na_2SO_3 to 3 of $NaHSO_3$ **H** is chiefly formed. **A**, obtained in 29.5 g. yield from 30 g. $p\text{-}O_2NC_6H_4NHAc$, crystals with 1 H_2O from 96% alc.; the benzidine, $C_{22}H_{10}O_2N_6(SO_3)_2$, and α - and β -naphthylamine salts also sep. with 1 H_2O . **B** (9-10 g. from 20 g. of the Ac acid refluxed 1 hr. with 3% $NaOH$) is white when freshly pptd. but turns blue rapidly in the air. **C**, $C_{19}H_{11}O_4N_4SO_3Na$ (7 g. from 5 g. **A** sapond. as above with $NaOH$ and heated 1 hr. on the H_2O bath in faintly alk. soln. with 10 g. $(O_2N)_2C_6H_3Cl$), red crystals from H_2O or alc., forms a difficultly sol. Ba salt. **D** (4 g. from 5 g. **B**), red ppt. Sodium *p*-benzoylamino-*o*-tolylsulfamate, obtained in 9 g. yield from 10 g. $Me(O_2N)C_6H_3NHBz$ after 15 hrs., crystals with 1.5 H_2O . **E** seps. with 1 H_2O and is sol. to the extent of 6.9% in H_2O (yield, 5-6 g. from 10 g. $O_2NC_6H_4NH_2$); β -naphthylamine salt, $C_{19}H_{11}N_2(SO_3)_2$. The azo dye obtained in 1.5 g. yield by diazotizing 2 g. **E** and coupling with β -naphthol is sol. in Na_2CO_3 and retains this property after boiling with acids. Sodium amino-*o*-tolylsulfaminisulfonate (3 g. from 5 g. $Me(O_2N)C_6H_3NH_2$), crystals with 0.5 H_2O . **F** (8 g. from 10 g. $o\text{-}O_2NC_6H_4NH_2$), crystals with 1 H_2O . Na salt of **G** (4 g. from 10 g. $C_6H_4(NO_2)_2$), pptd. in finely divided condition from 200 cc. alc. with 800 cc. H_2O and heated 7-8 hrs. with 90 cc. of 40% $NaHSO_3$, brownish crystals with 0.5 H_2O from boiling $EtOH\text{-}H_2O$; the mother liquors yield 2 g. of the di-Na salt of **H**, crystals with 3.5 H_2O from alc.

C. A. R.

Some acid derivatives of dinitriles and ethyl β -aminocrotonate. ERICH BERNARY AND MARTIN HOSENFELD. *Ber.* 55B, 3417-29(1922).— $(CO_2Et)_2$ (cf. *C. A.* 16, 1079) condenses with β -aminocrotonic nitrile in the presence of $NaOEt$, forming a *N*-deriv. while $(COC)_2$ in the presence of pyridine yields a *C*-deriv. Similar results are obtained in these expts., by the condensation of $PhOCH_2CO_2Et$ and $PhOCH_2COCN$ with dinitriles and *Et* β -aminocrotonate. Although E. v. Meyer considered the products obtained from the dinitriles with $PhOCH_2CO_2Et$ as true *C*-derivs., this series demonstrates the complete analogy between the phenoxyacetyl and the oxalyl derivs. The true *C*-derivs. when heated at 100° for 20 mins. with 3 parts $PhNHNH_2$ yield pyrazole derivs. on pptn. with $HOAc$. After heating with $NaOH$ at 100° for 20 min., the enol deriv. may be pptd. by the addn. of HCl . The *N*-derivs. either fail to react with $PhNHNH_2$ or yield $PhCONHNHPh$. Isomeric forms of their *Bz* and *Ac* derivs. may be sepd. Cinnamyl chloride condensed with diacetonitrile (**A**) gives both *C*- and *N*-derivs. With benzoacetodinitrile only the *C*-deriv. is formed, while in both cases the ester yields the normal *N*-compd. $ClCO_2Et$ couples with **A** in the presence of pyridine, forming $EtOOCNPhNiCMc:CHCN$ which ppts. on the addn. of H_2O ; recrystd. from $EtOH$, it m. $129\text{-}30^\circ$ (decompn.), is insol. in H_2O , Et_2O and petroleum ether, is unstable on standing or treating with HCl or $NaOH$. α -Phenoxyacetyldiacetonitrile, $MeC(NH_2)C(CN)\text{-}$

COCH_2OPh (B), from 5 g. A, 10 g. pyridine and drop-by-drop addn. of $\text{PhOCH}_2\text{COCl}$, pptd. with H_2O and recrystd. from EtOH—needles-m. 167° (decompn.), insol. in Et₂O and gasoline. α -Cyano- α -phenoxyacetyl-(enol)-acetone, $\text{MeC}(\text{OH})\text{:C}(\text{CN})\text{COCH}_2\text{OPh}$ (C), from B in 80% yield, needles from EtOH, m. 138° , insol. in H₂O and Et₂O, gives a characteristic color with FeCl_3 , forms a green Cu salt. 1-Phenyl-3-methyl-4-cyano-5-phenoxyethylpyrazole, from B or C, needles from dil. EtOH, m. $73\text{--}4^\circ$, insol. in H₂O. N-Phenoxyacetyldiacetonitrile, $\text{MeC}(\text{NHCOCH}_2\text{OPh})\text{:CHCN}$: α -deriv. m. 96° ; β -deriv. m. 123° . α -Phenoxyacetylbenzoacetodinitrile (D), plates from MeOH, m. 152° . α -Cyano- α -phenoxyacetyl-(enol)-acetophenone, from D, plates from EtOH, m. 118° . 1,3-Diphenyl-4-cyano-5-phenoxyethylpyrazole, from D, needles from EtOH, m. 158° , insol. in H₂O and Et₂O. N-Phenoxyacetylbenzoacetodinitrile, $\text{PhC}(\text{NHCOCH}_2\text{OPh})\text{:CHCN}$ (E), from benzoacetodinitrile and $\text{PhOCH}_2\text{CO}_2\text{Et}$; α -deriv. m. 95° (not 87° as given by Meyer); β -deriv. m. 114° ; warmed with NaOH or PhNHNH_2 both isomers decomp. The β -form yields a benzeneazo deriv., crystals from MeOH, m. 140° . α -Phenoxyacetyl-p-toluacetodinitrile (F), needles from EtOH, m. 178° . From F is obtained α -cyano- α -phenoxyacetyl-(enol)- β -methylacetophenone, crystals from EtOH, m. 141° . 1-Phenyl-3-tolyl-4-cyano-5-phenoxyethylpyrazole, crystals from EtOH, m. 167° . N-Phenoxyacetyl-p-toluacetodinitrile, $\text{MeC}_6\text{H}_4\text{C}(\text{NHCOCHOPh})\text{:CHCN}$, m. 148° , decomp. on warming with NaOH or PhNHNH_2 . α -Cinnamyl diacetone, $\text{MeC}(\text{NH}_2)\text{:C}(\text{CN})\text{COCH}\text{:CHPh}$ (G), prep. in the usual way with $\text{PhCH}\text{:CHCOCl}$, is sepd. from the simultaneously formed N-cinnamyl diacetone, $\text{MeC}(\text{NHCOCH}\text{:CHPh})\text{:CHCN}$ (H), by fractionation from MeOH or AcOH. G, needles, m. $198\text{--}9^\circ$, insol. in H₂O, petroleum ether and Et₂O, difficultly sol. in Me₂CO. H, quadratic plates, m. 192° , identical with the substance formed from $\text{PhCH}\text{:CHCO}_2\text{Et}$, KOEt and diacetone, decompd. by heating with NaOH or concd. H_2SO_4 , unchanged by heating with PhNHNH_2 or dil. H_2SO_4 . By the addn. of Br₂ in CHCl_3 , N- α -bromocinnamyl diacetone, $\text{MeC}(\text{NHCOBr}\text{:CHPh})\text{:CHCN}$, is formed; crystals from EtOH, m. $144\text{--}5^\circ$. The corresponding dibromide is apparently unstable. α -Cyano- α -cinnamyl-(enol)-acetone, from G, yellow needles from EtOH, m. 130° , stable to boiling with NaOH or HCl. 1-Phenyl-3-methyl-4-cyano-5-styrylpyrazole, from H with PhNHNH_2 , needles from EtOH, m. 134° , sol. in Me₂CO, C₆H₆, less in EtOH, MeOH, CHCl_3 , Et₂O, insol. in H₂O. α -Cinnamyl diacetone dibromide, $\text{MeC}(\text{NH}_2)\text{:C}(\text{CN})\text{COCHBrCHBrPh}$, from H by direct addn. of Br₂, needles from EtOH, darkening at 205° , m. 220° (decompn.). α -Cinnamylbenzoacetodinitrile (I), from $\text{PhCH}\text{:CHCOCl}$, benzoacetodinitrile, and pyridine, needles from EtOH, m. 173° , insol. in H₂O, Et₂O and gasoline, gives α -cyano- α -cinnamyl-(enol)-acetophenone, yellow needles from EtOH, m. 149° . 1,3-Diphenyl-4-cyano-5-styrylpyrazole, from I, crystals from EtOH, m. 205° (decompn.). N-Cinnamylbenzoacetodinitrile, formed from $\text{PhCH}\text{:CHCO}_2\text{Et}$, needles and plates from MeOH, m. $134\text{--}5^\circ$. Ethyl α -phenoxyacetyl- β -aminocrotonate, $\text{MeC}(\text{NH}_2)\text{:C}(\text{CO}_2\text{Et})\text{COCH}_2\text{OPh}$, from Et β -aminocrotonate, pyridine and $\text{PhOCH}_2\text{COCl}$, needles from EtOH, m. 159° , insol. in H₂O, Et₂O and gasoline, decomp. on warming with alc. KOH, NaOH, or H_2SO_4 . It forms 5-methyl-1-phenyl-3-phenoxyethylpyrazole-4-carboxylic acid, $\text{PhOCH}_2\text{C:N.NPh.CMe:CCO}_2\text{H}$, by boiling with PhNHNH_2 , and subsequent hydrolysis of the ester, needles from EtOH, m. 178° . Ethyl β -phenoxyacetylaminocrotonate, $\text{MeC}(\text{NHCOCH}_2\text{OPh})\text{:CHCO}_2\text{Et}$, from $\text{PhOCH}_2\text{CO}_2\text{Et}$, needles from EtOH, m. 88° , insol. in H₂O, Et₂O, and gasoline.

I. P. ROLF

Mechanism of the bromination of phenol in aqueous solution. HARRY BAINES. *J. Chem. Soc.* 121, 2810-3 (1922); cf. Dinwiddie and Kastle, *C. A.* 6, 482.—When treated with the theoretical amt. of Br, PhOH in CCl_4 gives the o- and p- $\text{BrC}_6\text{H}_4\text{OH}$ or 2,4- $\text{Br}_2\text{C}_6\text{H}_3\text{OH}$. If H₂O be added to the mixt., $\text{Br}_2\text{C}_6\text{H}_3\text{OH}$ is immediately formed in the aq. layer and redissolves in the CCl_4 . The degree of moisture of the solns. has an effect

on the velocity of the reaction. The facts are explained on the assumption that the slow reaction between dry PhOH and dry Br in an inert solvent is one of direct substitution, while the rapid bromination of PhOH in H₂O is due to the action of HOBr, formed by the interaction of Br and H₂O. The HOBr probably reacts with the PhOH by addn. with subsequent elimination of H₂O. This was confirmed by the direct action of HOBr upon PhOH, and the mechanism is further supported by the fact that the bromination is retarded by conditions hindering the formation of HOBr. C. J. WEST

New derivatives of *p*-phenetylurea (dulcin). M. BERGMANN, F. CAMACHO AND F. DREYER. *Ber. pharm. Ges.* 32, 249-58 (1922).—The main object of this investigation was the prepn. of new derivs. of dulcin having greater soly. and equal or greater sweetening power. The following substances are described. *Methylphenetylurea*, EtOC₆H₄NMeCONH₂, from *N*-methylphenetidine-HCl and KCNO, needles, m. 128-9°, equally sweet but less pleasant than dulcin, soly. 220 times greater. *N-Hydroxyethyl-N-phenetylurea*, EtOC₆H₄N(CH₂CH₂OH)CONH₂, needles, m. 113-5°, easily sol. in H₂O, sweeter than dulcin but less pleasant. *Dihydroxypropylphenetylurea*, EtOC₆H₄N[CH₂CH(OH)CH₂OH]CONH₂, crystals, m. 138-9°, easily sol. but without sweetness. *N-Phenetyl-N-carbethoxymethylurea*, EtOC₆H₄N(CH₂CO₂Et)CONH₂, needles, m. 86-7°, soly. in H₂O very slight, taste faintly bitter without sweetness. *N-Phenetyl-N-allylurea*, EtOC₆H₄NHCONHCH₂CH=CH₂, from phenetidine and C₆H₅CNS and subsequent treatment with HgO, rectangular plates, m. 157°. *N-Phenetyl-N'-methylurea*, EtOC₆H₄NHCONHMe, rectangular plates, m. 159°. *N-Phenethyl-methyl-N'-methylurea*, EtOC₆H₄NMeCONHCH₃, prisms, m. 94-5°. *N-Phenethyl-methyl-N'-allylurea*, EtOC₆H₄NMeCONHCH₂CH=CH₂, needles, m. 57-8°. The 4 preceding compds. are all very difficultly sol. and possess no distinctly sweet taste. W. O. F.

Interaction of diazonium salts and phenols. F. D. CHATTAWAY AND H. R. HILL. *J. Chem. Soc.* 121, 2756-60 (1922).—The first product of the reaction which takes place when a soln. of a diazonium salt is added to an alk. soln. of a phenol consists of an additive compd. RON₂Ar, which changes in the 2nd part into a mixt. of the *o*- and *p*-hydroxy-azo isomerides. Both of these by similar addn. and intramol. change yield the hydroxy-2,4-bis- and finally the hydroxy-2,4,6-trisazo compd. *p*-ClC₆H₄N₂Cl and PhONa give 99% of the *p*-azo deriv. and 1% *q'*-chloro-2-benzenesazophenol, long, very slender, bright reddish orange prisms, m. 117.5°. *q'*-Bromo derivative, in 0.6% yield, slender, bright reddish-orange prisms, m. 133.5°. *q'*-Iodo derivative, in 0.6% yield, long, very slender, needle-like prisms of bright scarlet color, m. 139°. *2-o*-Toluenesazophenol, obtained in 0.4% yield, forms long, very slender, needle-shaped, golden red crystals, m. 88°. The hydroxybisazo compds. are easily made by adding a soln. of a diazonium salt to an alk. soln. of either a HO-*o*- or a HO-*p*-azo compd. and subsequently acidifying. *4',4''*-Dichloro-2,4-bisbenzenesazophenol, nodular aggregates of brown microcrystals, m. 210-1° (decompn.). *4',4''*-Dibromo derivative, yellowish brown cryst. nodules, m. 224° (decompn.). *4',4''*-Diiodo derivative, dark brown aggregates, m. 208°. *4-p*-Chlorobenzenesazo-2-benzenesazophenol, yellow-brown microcrystals, m. 165°; *4-p*-bromo derivative, aggregates of brown microcrystals, m. 178°; *4-p*-iodo derivative, dark brown microcrystals, decomp. at about 160°. *2-p*-Chlorobenzenesazo-4-benzenesazophenol, yellow, m. 133°; *2-p*-bromo derivative, brown microcrystals, m. 147°; *2-p*-iodo derivative, nodules of dark brown microcrystals, m. 119°. *2-p*-Bromobenzenesazo-4-*p*-toluenesazophenol, aggregates of light brown microcrystals, m. 192°. *4-p*-Bromobenzenesazo-2-*p*-toluenesazophenol, m. 213°. The trisazo compds. have not been isolated as they are difficult to free from the bis-compds. C. J. WEST

Action of bromine on nitrophenolsulfonic and sulfonic-carboxylic acids. EUKLID SAKELLARIOS. *Ber.* 55B, 2846-53 (1922).—In the present paper are described a no. of instances of the quite smooth replacement of SO₃H and CO₂H groups by halogen. Thus,

1,2,4,6- $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)(\text{SO}_3\text{H})_2$, or, better, its di-K salt (A), treated with 1 mol. Br in H_2O , gives quant. the K salt of 2-nitro-6-bromophenol-4-sulfonic acid (B), which with a 2nd mol. of Br gives 4,6,2- $\text{Br}_2(\text{O}_2\text{N})\text{C}_6\text{H}_2\text{OH}$ (C) and with concd. HNO_3 6,2,4- $\text{Br}(\text{O}_2\text{N})_2\text{C}_6\text{H}_2\text{OH}$. Reduction of 34 g. B gives 23 g. of the 2-amino acid. Similarly, 1,2,6,4- $\text{C}_6\text{H}_2(\text{OH})(\text{NO}_2)_2\text{SO}_3\text{H}$ quant. gives 4,2,6- $\text{Br}(\text{O}_2\text{N})_2\text{C}_6\text{H}_2\text{OH}$, m. 78° (cf. Körner, *Jahresber.* 1875, 336), not 85.6° as given in Beilstein and in Richter's *Lexikon*. Hirsch's nitrosulfosalicylic acid (*Ber.* 33, 3238(1900)) gives B with Br and is therefore 3-nitro-2-hydroxybenzene-1-carboxylic-5-sulfonic acid. A is obtained in 140 g. yield by direct pptn. with KCl from the dild. nitration mixt. contg. the acid instead of first isolating the acid through the Ba salt (Chamot and Pratt, *C. A.* 4, 1726); with Zn dust and HCl it gives monopotassium 2-aminophenol-4,6-disulfonate, crystals with 1 H_2O which it does not lose at 160° , soon becomes reddish in the air. The statement of Datta and Mitter (*C. A.* 14, 182) that bromination of 1,2,4- $\text{C}_6\text{H}_3(\text{OH})(\text{NO}_2)\text{SO}_3\text{H}$ gives C is not entirely correct, for with 1 mol. Br 25.4 g. of the Na salt gives 31 g. of the K salt of B. C. A. R.

Residual affinity and coordination. XII. Cobaltamine and ferric lakes of dinitrosoresorcinol. G. T. MORGAN AND J. E. MOSS. *J. Chem. Soc.* 121, 2857-66 (1922); cf. *C. A.* 17, 37, 534.—The presence of chelate groups in a dye may be detected by the use of an NH_4OH soln. of $[\text{HOCO}(\text{NH}_2)_2]\text{Cl}_2$ (A). Applying this test to $(\text{O}_2\text{N})_2\text{C}_6\text{H}_2(\text{OH})_2$, or 1,2,3,4-benzodiquinone-1,3-dioxime (B), it is found that it behaves like a monochelate dye; this substantiates the consecutive formula, the median :NO group being involved in the chelating complex while the terminal :NO group situated in the *p*-position with respect to the remaining CO group behaves merely as an acidic radical. The interaction of an NH_4OH soln. of B with A gave 1-pentamminocobaltic 3-cobaltic 1,2,3,4-benzodiquinone-1,3-dioximate, $(\text{C}_6\text{H}_2\text{O}_4\text{N}_2)_2\text{Co}_2(\text{NH}_3)_8$, which 1st ppts. as the trihydrate, chocolate-brown, and is freed of H_2O by drying over CaO for 3 days, forming a chocolate-brown, amorphous powder insol. in H_2O and the ordinary org. media. With cold, concd. HCl, HNO_3 or H_2SO_4 the anhydrous lake developed a reddish brown color, becoming orange on dild. A partly chelated lake, $(\text{C}_6\text{H}_2\text{O}_4\text{N}_2\text{H}_2\text{O})_2\text{Co}_2(\text{NH}_3)_8$, was also prepd. The basic Fe''' lake, 1-ammonium 3-hydroxyferric 1,2,3,4-benzodiquinone-1,3-dioximate, $(\text{C}_6\text{H}_2\text{O}_4\text{N}_2)_2\text{FeOH}$, was obtained from $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ and B in NH_4OH , black amorphous powder, giving a dark green aq. soln. Concd. HNO_3 or H_2SO_4 gave a reddish brown color. Boiling with concd. HCl gave a soln. showing the reactions of Fe''' . The normal Fe''' lake, 1-ammonium 3-ferric derivative, $(\text{C}_6\text{H}_2\text{O}_4\text{N}_2\text{NH}_4)_2\text{Fe}$, was prepd. from Fe''' alum and forms a bluish black powder sol. in H_2O or $\text{C}_2\text{H}_5\text{N}$ to a dark green soln. FeCl_3 and B in $\text{C}_2\text{H}_5\text{N}$ gave a ppt. after the addn. of EtOH which analyzed for a ferric pyridine lake, $(\text{C}_5\text{H}_5\text{N}\cdot\text{NO}\cdot\text{C}_6\text{H}_2\text{O}_4\cdot\text{NO})_2\text{FeOH}$. 4 $\text{C}_2\text{H}_5\text{O}$, dark green, sparingly sol. in H_2O but sol. in $\text{C}_2\text{H}_5\text{N}$. 3,6-Dipentamminocobaltic 1-cobaltic 8-amino-1-oxynaphthalene-3,6-disulfonate, $(\text{C}_{10}\text{H}_6\text{ONH}_2\text{SO}_3)_2\text{Co}_2(\text{NH}_3)_{10}$, from H acid, chocolate-brown amorphous product, sol. in H_2O with a reddish brown color and changing to carmine on addn. of NaOH or to yellow on acidifying. It developed a heliotrope color, changing to carmine, with concd. H_2SO_4 . 2,4- $\text{H}_2\text{N}(\text{HO}_2\text{S})\text{C}_6\text{H}_2\text{OH}$ gave only a partly chelated compound, $(\text{C}_6\text{H}_2\text{ONH}_2\text{SO}_3\text{H}_2\text{O})_2\text{Co}_2(\text{NH}_3)_8$, brown ppt. Anthranilic acid gave only a cobaltous salt, $(\text{C}_7\text{H}_5\text{O}_2\text{N})_2\text{Co}$, amorphous gray powder. XIII. Cobaltamine and chromic lakes of the azosalicylic acids. G. T. MORGAN AND J. D. M. SMITH. *Ibid* 2866-74.—The azosalicylic acids are shown to contain a chelate group analogous to that present in alizarin, being composed of the HO and the contiguous CO radicals of the salicylate residue; the other HO group acts as a salt-forming group. Six mordant dyes of this series have been exam'd. Structural formulas for the lakes are given in the original. Pentamminocobaltic *m*-nitrobenzeneazosalicylate, $(\text{C}_{13}\text{H}_7\text{O}_4\text{N}_2)_2\text{Co}_2(\text{NH}_3)_8$, dark buff, amorphous ppt., developing intense red colors in Me_2SO and all concd. acids. Bisagupentamminocobaltic derivative, brown ppt., sol. in Me_2SO or concd.

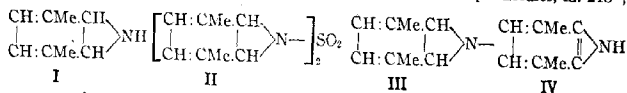
acids with a yellow color. On boiling with H_2O , the salt lost half its NH_3 in 15 min., passing into the above chelated lake. The latter is stable in boiling NH_4OH , although it is appreciably unstable in boiling H_2O . The *bis*hexamminocobaltic salt, $(C_{10}H_7O_2N_6)_2[Co(NH_2)_6]_2 \cdot 5H_2O$, is buff-yellow and develops an orange-yellow color with Me_2SO_4 or concd. acids. *Pentamminodibaltic p-nitrobenzenesalicylate*, reddish chocolate, sol. in Me_2SO_4 with an intense red color and evolving NH_3 when heated with 5 *N* $NaOH$, giving a red soln. *3,3'-Dipentammino-3,4,3'-tricobaltic benzene-1-azo-4-oxybenzene-3,3'-dicarboxylate*, $[(C_{14}H_7O_2N_5)_2Co]_3[Co(NH_2)_5]_3$, khaki-brown ppt., which slowly evolves NH_3 on standing and is sol. in Me_2SO_4 with an intense red color. *2,3'-Dipentammino-2',3,4-tricobaltic benzeneazo-4-oxybenzene-2',3-dicarboxylate*, reddish brown. *3',6,8-Tripentammino-3',4',6,8-tetracobaltic 6,8-disulfonaphthalene-2-azo-4'-oxybenzene-3'-carboxylate*, $[(C_{17}H_5O_2N_5S_2)_2Co]_4[Co(NH_2)_5]_4$, dark brown microcryst. ppt., sol. in H_2O or dil. alkali to a brownish yellow or reddish orange soln., in dil. acids to a reddish purple soln., and in Me_2SO_4 and concd. acids to an intense carmine-red soln., becoming purple and orange on diln. *Dichromic m-nitrobenzenesalicylate*, by adding the $NaOH$ soln. of the acid to Cr alum, lemon-yellow, changed to a brick-red by concd. HCl or H_3PO_4 . *3-Pentammino-2,3-dicobaltic m-nitrobenzene-1-azo-2-oxy-3-naphthoate*, from *m-nitrobenzene-1-azo-2-hydroxy-3-naphthoic acid* (Cu-red needles, m. $271-3^\circ$), brownish red. *Pentammino-1,2-dicobaltic 2-oxybenzoate*, $(C_7H_4O_2)_2Co_2(NH_2)_5(H_2O)_3$, sage-green powder, giving a brown soln. with Me_2SO_4 and concd. acids. **XIV. Interactions of metallic salts and dimethyldithiolethylene.** G. T. MORGAN AND WILFRID LEDBURY. *Ibid* 2882-94.—The results show that there is at least a qual. relationship between the tendency for a metallic radical to combine with S by principal or electronic valences and its propensity to become associated with alkyl sulfides. In certain instances the metallic radical pptd. as sulfides in analytical practice give rise to well defined coordination compds. with dimethyldithiolethylene (A). Whenever the analytical procedure tends to produce an alteration in the valency of the metallic radical a similar tendency is observable with the dithiol deriv.; diminution in valency is noticed with Cu and Au, whereas an exaltation of valency accompanied by partial elimination of metal is indicated in the case of Hg' salts. Of the metals examd. those forming the most refractory sulfides furnish the most stable dithiol coordination products. *Bis-A cuprous bromide*, formed by adding A to $CuSO_4$ in H_2O and then adding KBr , 6-sided plates, m. $161-2^\circ$ (decompn.), and sol. in C_6H_5N to a bright yellow soln., becoming olive-green on heating. *Bis-A cupric chloride*, pptd. by $EtOH$ from dil. $EtOH-HCl$ as dark green acicular crystals, m. $130-30.5^\circ$. A *bisaurous chloride*, rod-like microcrystals, blackening without m. $178-9^\circ$. A *auric chloride*, small orange-yellow, acicular crystals, decomp. $70-5^\circ$, and converted into the aurous deriv. by H_2O . A *zinc bromide*, aggregates of small, hard octahedral crystals, m. 137° . A *cadmium iodide*, glistening needles from $EtOH$, m. $168-9^\circ$. A *mercurous nitrate*, formed, with the simultaneous sepn. of Hg, as very small, nacreous prisms, decomp. violently 156.5° . A *mercuric chloride*, hard prisms, m. 109° (decompn.). A *mercuric bromide*, acicular crystals, m. 115° . A *mercuric iodide*, matted needles from $EtOH$, becoming yellow at $126-7^\circ$ and m. 134° (decompn.). It is sol. in hot H_2O without dissociation. A *stannic chloride*, m. 209° (decompn.). A *stannic bromide*, yellowish white, becoming yellow on heating and m. 199° (decompn.). A *stannic iodide*, m. 100° . *Tris-A dibismuthotri-iodide*, bright scarlet, m. $85-7^\circ$. This is very sensitive to light or moist air; digestion with cold org. solvents gave *di-A bis-muth iodide*, black. A *palladous chloride*, short, lustrous yellow needles, m. $234-5^\circ$ (decompn.). $AgNO_3$ gives a ppt. of $AgCl$, with the formation of the *palladous nitrate*, yellow, m. 162° . Aq. NH_3 decompd. the chloride, forming $(NH_3)_2PdCl_2$. Warm dry C_6H_5N also decompd. the chloride, liberating A and on concn. the soln. gave a *substance*, $(C_6H_5N)_4PdCl_2$, which lost C_6H_5N over H_2SO_4 , giving *dichlorodipyridinopalla-*

dium, $(C_6H_5N)_2PdCl_2$. A palladous bromide, from the chloride and KBr, small, orange-yellow needles, m. $219-20^\circ$ (decompn.). A palladous iodide, dark red, acicular crystals, m. 204° (decompn.). CS_2 and Tl acetylacetone (B) or benzoylacetone react to give ill defined products in which approx. 0.5 of the acetylacetone has been replaced by CS_2 , $(Tl_2CH(COMe)_2SC_2(?))$, but it is impossible to arrive at a rational formula. B reacts with $\alpha-C_6H_5SH$, giving the yellow Tl salt of the latter and free CH_3Ac_2 . With concd. solns. of B and thiophene a small amt. of Tl_2S was pptd. With concd. alc. solns. of thiophene and $TiOH$, black Ti_2S_3 was rapidly pptd., and the filtrate, after exposure to the air, yielded a small proportion of $(-CH_3CO_2Ti)_2$. C. J. WEST

Synthesis of some primary alcohols from monomolecular formaldehyde and Grignard reagents. KARL ZIEGLER AND PAUL TIEMANN. *Ber.* 55B, 3406-17(1922); cf. C. A. 15, 3090.—A no. of new primary carbinols are prepd. in a slightly modified form of the app. previously described. 50 g. $1,4-C_{10}H_8MeBr$ in 250 cc. abs. Et_2O is boiled 1 hr. with 11 g. activated Mg and $HCHO$ from 14 g. $(CH_3O)_2$ introduced. A 40% yield of 1-methyl-4-hydroxymethylnaphthalene (A), crystals from C_6H_6 , m. $74-5^\circ$, sol. in $EtOH$, Et_2O and less in gasoline, is obtained. Its phenylurethan m. 103° . Oxidation with 2 N $K_2Cr_2O_7-H_2SO_4$ at 60° , yields 84% 1-methyl-4-naphthaldehyde, b_{11} $174-6^\circ$; purified through the $NaHSO_3$ compd., and crystd. from gasoline, it m. $33.5-4^\circ$. Semicarbazone, plates from $EtOH$, m. 228° . Azine, crystals from $EtOH$, m. $136-7^\circ$. 2-Methyl-1-hydroxymethylnaphthalene (B), prepd. in 85% yield, recrystd. from $EtOH-C_6H_6$, m. $136-7^\circ$. Phenylurethan m. $127-8^\circ$. On satn. of an $HOAc$ soln. of B with HCl , 2-methyl-1-chloromethylnaphthalene crystals, plates from $MeOH$ or $HOAc$, m. $61-3^\circ$. The analogously prepd. 2-methyl-1-bromomethylnaphthalene, m. $87.5-9^\circ$. B cannot be directly oxidized to the aldehyde; the latter is formed in traces from C and D by reacting with hexamethylenetetramine (Sommelet). D on standing 3 days in moist Et_2O with 2 parts Na, to which H_2O is added in drops from time to time, forms tetrahydro-1,2-dimethylnaphthalene contaminated with traces of the dihydro deriv. From $Ph_3C:CHBr$, γ -phenylcinnamyl alcohol (E) is formed, isolated as the phthalic ester. E , b_{11} 205° , b_{12} 192° , crystals from gasoline-MeOH, m. $61.5-3.0^\circ$. The acetate b_{11} 205° , m. $36-7^\circ$, d_4^{20} 1.1003, d_4^{20} 1.091, n_D^{20} 1.5817. Benzoate, from E (Schotten-Baumann), crystals from $MeOH$, m. $89-90^\circ$. On reduction of E with Na, Ph_3CHI is formed 3,3-Diphenylallyl bromide, prepd. from E by addn. of HBr in $HOAc$, and extn. with Et_2O , crystals from $MeOH$, m. $37-9^\circ$, converted to γ -phenylcinnamaldehyde (Sommelet), identified as the semicarbazone m. $214-5^\circ$. γ -Phenyl- β -methylcinnamyl alcohol (F), b_{11} 184° , prisms from gasoline, m. $68-9^\circ$. Its benzoate m. 116° . 2 g. F in 20 cc. $HOAc$ to which is added 5 cc. H_2SO_4 in $HOAc$ forms γ -phenyl-2-methylindene, b_{11} $172-80^\circ$, from $HOAc$ m. 56.5° . p -Bromobenzyl alcohol (G), prepd. from $p-C_6H_4Br_2$ (60% yield), is found in the fraction b_{11} $125-40^\circ$. Oxidized with $K_2Cr_2O_7-H_2SO_4$, it gives 87% of p - BrC_6H_4CHO (H), b_{12} $105-10^\circ$, m. 57° . From H and $MgBrMe$ is obtained p -bromophenylmethylcarbinol (I), a colorless oil of burning taste, b_{11} $133-4^\circ$, b_{12} $127-8^\circ$, d_4^{20} 1.463, n_D^{20} 1.5697. From I, by heating for 1 hr. at 150° with freshly melted $NaHSO_4$, pouring into H_2O , and extg. with Et_2O , a mobile oil of characteristic odor, solidifies 4.5° , d_4^{20} 1.401, n_D^{20} 1.5961, M_D 44.36, identified by the addn. of Br_2 , forming α,β - p -tribromoethylbenzene, m. $60-1^\circ$. p -Bromophenylethylcarbinol, $C_8H_8BrCH(OH)Et$ (J), from p - BrC_6H_4CHO and $MgBrEt$, b_{11} $138-9^\circ$, d_4^{20} 1.404, n_D^{20} 1.5607. p -Bromopropenylbenzene, $C_8H_8BrCH:CHMe$, m. 35° , has a pleasant odor, does not polymerize as easily as p -bromostyrene, b. $238-9^\circ$, b_{11} $108-10^\circ$, d_4^{20} 1.356, n_D^{20} 1.5934, M_D 49.53. Its dibromide m. $61-3^\circ$. p -Bromoisopropenylbenzene, $C_8H_8BrCMe:CH_2$, formed by direct dehydration of the reaction product of p - BrC_6H_4MgBr and Me_2CO , b. 228° , b_{11} 110° , solidifies 11° , d_4^{20} 1.350, n_D^{20} 1.5835, M_D 48.71. A solid dibromide could not be prepd. More extensive phys. consts. of the styrenes are given.

I. P. ROLF

Action of sulfonyl azide, $N_2SO_2N_3$, on *p*-xylene. THEODOR CURTIUS AND FRIEDRICH SCHMIDT. *Ber.* 55B, 1571-81 (1922).—While the azides of org. (especially aromatic) SO_2H acids are generally substances which can be handled without danger, $N_2SO_2N_3$ has exceedingly explosive, unpredictable properties; in many cases very violent explosions occurred without any apparent reason, and in others contact with metals seemed to be the factor detg. the explosion. With hydrocarbons (*p*-xylene was used) it behaves differently from most sulfonazides. During the heating there is evolved not only N_2 but also considerable SO_2 (more than $\frac{2}{3}$ of the total S is split off in this form); from the beginning of the N_2 evolution the soln. becomes yellow-brown and there sep. brown products whose amt. gradually increases during the long heating. On moistening with NaOH these evolve a powerful C_3H_5N odor; together with undefined humus-like substances they contain the sulfates of 3 bases (A, B and C) and from the mother liquors of the picrates of these bases can be isolated a neutral substance (D). A, which is isomeric with xylidine and is called *pseudoxylidine*, is believed to have the structure I; probably the $N_2SO_2N_3$ forms a residue $=NSO_2N=$ which adds 2 mols. xylene with formation of the compd. II which, losing SO_2 , yields the residue III, and an exchange of H occurs between the III with formation of I and IV. B is supposed to have the structure IV; as to the structures of C and D, which are isomeric with B, nothing can as yet be said. From 50 g. $N_2SO_2N_3$ in 3% xylene soln. slowly raised in the course of a week to the b. p. until the evolution of gas ceases, filtered, freed from adherent xylene with steam, made alk., distd. with steam, treated with HCl and evapd. *in vacuo* is obtained 4 g. of a mixt. of HCl salts; the non-volatile residue from the alk. soln. yields a little HN_3 and 4 g. H_2SO_4 . The bases liberated from the HCl salts with alkali, taken up in Et_2O and distd. yield an oil from which sep. crystals of the solid C; the remaining oil with picric acid in Et_2O yields a mixt. of the picrates of A and B, sep'd. by fractionation from alc. The *hydrochloride* of A forms very hygroscopic, not very strongly doubly refractive, radiating star- and feather-like crystals yielding NH_4Cl on repeated evapn. with HCl; the *chloroplatinate* seps. in 2 forms (probably *cis-trans* isomers), light yellow anisotropic platelets, m. 148° , and dark yellow crystals, m. 181° (decompn.); *picrate*, doubly refractive platelets, m. 152° . *Hydrochloride* of B, non-hygroscopic, strongly doubly refractive, vividly anisotropic spears and plates, also NH_4Cl -like formations, m. $212-3^\circ$, forms NH_4Cl when repeatedly evapd. with HCl; *chloroplatinate*, tables, m. 260° ; *picrate*, strongly doubly refractive prisus, m. 239° . The base C seps. in strongly doubly refractive stars or platelets, reacts strongly alk. to litmus; *hydrochloride*, long, strongly anisotropic, non-hygroscopic, prismatic platelets, m. 218° ; *picrate*, yellow anisotropic needles, m. 218° ;



chloroplatinate, light yellow strongly doubly refractive platelets, m. 242° , and dark yellow crystals, m. 181° (gas evolution). The compound D forms anisotropic needles and tables, m. 85° , insol. in HCl.

C. A. R.

Action of sulfonyl azide on benzene. FRIEDRICH SCHMIDT. *Ber.* 55B, 1581-3 (1922); cf. preceding abstr.—In order to make sure that in the reaction between $N_2SO_2N_3$ and xylene the Me groups do not take part, C_6H_6 was substituted for the xylene. The evolution of N is so extraordinarily slow in boiling C_6H_6 , however, that the reaction was carried out under compressed CO_2 in an all-glass autoclave provided with a safety valve set for about 4 atm., which permitted of heating the soln. to about 140° . Unlike the product obtained with xylene, the base isolated in this case from the brown humus-like product proved to be a homogeneous *pseudoaniline*, whose *picrate* m. 163° .

C. A. R.

Hexamethyleneimine and its behavior on oxidation. FRIEDRICH SCHMIDT. *Ber.*

55B, 1584-91(1922).—Desiring to prep. hexamethinimine (A), $\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2 \\ || \\ \text{CH}_2\text{CH}_2\text{CH}_2 \end{array} \text{NH}$.

isomeric with the pseudoaniline described in the preceding abstr., S. undertook to oxidize hexamethyleneimine (B) and finally succeeded, by heating in a sealed tube with AgOAc, in obtaining a definite product but this proved to be α -picoline (C) instead of A. Hexamethylenediamine (D) was prepd. by the method of Curtius and Clemm (*J. prakt. Chem.* 62, 189(1900)); instead of hexamethylenedi[ethylurethan], hexamethylene diisocyanate can be used equally well for its prepn.; this compd., oil of penetrating odor, b. 225°, is obtained in 66% yield from suberic diazide refluxed 8 hrs. in dry Et₂O and on boiling with concd. HCl yields D rapidly and smoothly. D, 2HCl in 5-10-g. portions heated in a large flask over a free flame at such a temp. that NH₄Cl is split off and condenses on the upper, cooler parts of the flask gives about 50% B, mobile liquid of strong piperidine-like odor, b. 126-7°, is not miscible in all proportions with H₂O, a soln. satd. at 15° sepg. into 2 layers on warming, d₄ 0.829, mol. wt. (dett. by the Hofmann vapor density method) 97.4; picrate, stout light yellow crystals, m. 85° (previously obtained only as an oil); HCl salt, very hygroscopic, doubly refractive radiating prisms and NH₄Cl-like formations; chloroplatinate, slender platelets, m. 191° (v. Braun describes a salt with 1 H₂O as long needles m. 148°). The identity of B with v. B.'s product was further confirmed by converting it into the tetra-Mc deriv., m. 214°, and its chloroplatinate, m. 248° (decompn.). Boiled in Et₂O with Ac₂O it gives an acetyl derivative, b. 239-41°, easily sol. in H₂O, repptd. by concd. KOH, saponid. by alkalis only on long boiling, much more rapidly by boiling acids. C. A. R.

Reduction of substituted salicylic acids. HUGO WEIL, MAX TRAUN AND SIGISMOND MARCEL. *Ber.* 55B, 2664-74(1922).—The 3 cresotic acids reduced in the manner already described (15.2 g. acid and about 6 g. Na₂CO₃ in 1 l. H₂O, 10 g. H₃BO₃ and 90 g. of com. 40% NaHSO₃ (nearly neutralized to litmus with NaOH) treated in the course of 5-6 hrs. with 200 g. of 3.5% Na-Hg in 10-5-g. portions) yield about 33% of the corresponding aldehydes, and 7-8 g. of the acids are recovered unchanged. 5-Chlorosalicylic acid, obtained in 7-8 g. yield from 10 g. 5,2-ClH.H₂N(HO)C₆H₃CO₂H by the Sandmeyer method, sublimes in needles, m. 167.5°; 8.5 g. on reduction gives 1.7 g. of the aldehyde, m. 99.5°, and 3 g. of the acid are recovered. The 5-Br acid (10.5 g.) gives 1.1 g. of the aldehyde, m. 104-5°, and 4 g. unchanged acid, and from 15 g. of the 3,5-Br₂ acid are obtained 0.8 g. of the aldehyde, m. 85°, and 10 g. unchanged acid. With hydroquinol- and pyrogallolcarboxylic acids there is much foaming and the acids are recovered quant., but 5 g. resorcylic acid gives 1 g. of the aldehyde, yellow crystals, m. 134-5°, and no unchanged acid. 5,2-ClH.H₂N(HO)C₆H₃CO₂H (obtained in 80-90% yield from the NO₂ acid with Zn dust and HCl) on reduction as above yields no aldehyde, on extn. with Et₂O or distn. with steam but strongly reduces Fehling and Ag solns. (the latter with mirror formation) and with NaOH gives about 60% of the N as NH₃; with PhNHNH₂ and NaOAc is obtained a phenylhydrazine derivative, straw-yellow leaves from MeOH, m. 151°, which gradually decomp., especially on heating or *in vacuo* and in sunlight, and when rubbed with concd. HCl changes, without dissolving, into a stable cryst. hydrochloride, the compn. of which shows that besides the reduction of the CO₂H group to CHO, a hydrogenation of the nucleus has also occurred, that 2 mols. PhNHNH₂ have combined with 1 of the original acid and that the NH₂ group has been eliminated, so that the product of the reduction (A) was believed to be hexahydrosalicylaldehyde (B); *p*-nitro- and *p*-bromophenylhydrazine derivatives. In a continuation of this work it was found that 5,2-H₂N(HO)C₆H₃CHO (C), is also always formed to a greater or smaller extent (as much as 16%); it has not yet been established what conditions are favorable or unfavorable to its formation. A is extraordinarily sol. in H₂O and can be

removed with Et_2O only after several days' extn.: evapn. of the Et_2O leaves a thick oil smelling strongly of green tobacco leaves, attacking the mucous membranes, turning the skin brown, producing a strong burning sensation on the tongue, and quickly polymerizing to an almost white solid insol. in H_2O and org. solvents; with $\text{H}_2\text{NCONHNH}_2$ it yields a bissemicarbazone (D), and is therefore not B but the isomeric *pinelic dialdehyde*. C was also prepd. by reduction, best with H_2S in a soln. faintly alk. with Na_2CO_3 , of azo dyes derived from *o*- $\text{HOC}_6\text{H}_4\text{CHO}$; it seps. as a voluminous red ppt., evidently a polymer, sol. only in traces in org. solvents but reacting with chem. agents in the monomol. form; the latter could not be isolated; dil. HCl solns. remain clear and yellow for a time after the addn. of a slight excess of Na_2CO_3 but after a while deposit the red polymeric form; long extn. of this with Et_2O gives yellow solns. of the monomol. form but the red polymer is again formed on evapn.; the light yellow soln. in dil. HCl deposits on addn. of concd. HCl the fiery red polymeric *hydrochloride* which is no longer completely sol. in H_2O , owing to partial dissociation. *5-Benzeneazosalicylaldehyde-4'-sulfonic acid*, from $\text{HOC}_6\text{H}_4\text{CHO}$ and diazotized $\text{H}_2\text{NC}_6\text{H}_4\text{SO}_3\text{H}$. The *phenylhydrazone* of C, when freshly prepd. and still moist, is easily sol. in H_2O and most org. solvents and seps. from MeOH in crystals, m. 263° (decompn.); after drying it loses this soly. but is still sol. in dil. alkali and CO_2 ppts. from this soln. another form, m. 160° , which is easily sol. in org. solvents after drying and seps. from C_6H_6 -ligroin in light yellow flocks, m. $184-5^\circ$ (decompn.); *semicarbazone*, m. above 300° (decompn.). In the later work, the m. p. of the bisphenylhydrazone of B was raised to 157° ; the bis-*p*-nitrophenylhydrazone m. 204° . D, $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}_6$, m. 237° (decompn.). C. A. R.

Formation of γ -alkylidene derivatives from ethylidenemalonate ester. LUCY HIGGINBOTHAM, ARTHUR LAPWORTH and CHAS. SIMPSON. *J. Chem. Soc.* 121, 2823-30 (1922).—Reasons are given for the view that the capacity of esters like Et crotonate to condense with $(\text{CO}_2\text{Et})_2$ and aldehydes in the γ -position is really conditioned by the presence of the group $-\text{CH}_2\text{C}=\text{C}-$, or perhaps more generally of the group $-\text{CH}:\text{A}:\text{B}=-$, and the supposition that the reactivity of this group is usually insufficient unless enhanced by duplication within a ring or by induced polarity effects. $\text{MeCH}:\text{C}(\text{CO}_2\text{Et})_2$ and BzH condense to give $\text{PhCH}:\text{CHCH}:\text{C}(\text{CO}_2\text{Et})_2$ in a 50% yield. *p*- $\text{MeOC}_6\text{H}_4\text{CHO}$ gave *p*-methoxycinnamylidenemalonate acid, orange needles, m. 189° (decompn.). It decolorized KMnO_4 , giving *p*- $\text{MeOC}_6\text{H}_4\text{CHO}$, and lost CO_2 when heated *in vacuo*. Piperonal and $\text{MeCH}:\text{C}(\text{CO}_2\text{Et})_2$ gave a mixt. of acids in which piperonylenemalonate acid was identified through conversion into piperic acid by boiling with Ac_2O . Evidence of the condensation of other aromatic aldehydes has been obtained but the nature of the products is as yet uninvestigated. Expts. on $\text{MeCH}(\text{OEt})_2$, *m*- $\text{MeOC}_6\text{H}_4\text{Me}$ and 3,5-(MeO) $_2\text{C}_6\text{H}_3\text{Me}$ with aldehydes, $(\text{CO}_2\text{Et})_2$, and alkyl nitrites were negative. C. J. WEST

Tannins and similar compounds. XI. Chinese tannin. KARL FREUDENBERG and WILHELM SCHLÄGL. *Ber.* 55B, 2813-6(1922); cf. C. A. 17, 744.—It in (C. A. 8, 2378) succeeded in sepg. com. Chinese tannin into a portion with high rotation ($[\alpha]_D^{137}$ in H_2O) and one of low rotation (5° and less). His observation having been confirmed with a com. sample, F. and S. prepd. their own tannin by quickly exhausting rushed Chinese galls with hot H_2O , concg. the turbid exts. *in vacuo*, neutralizing with Na_2CO_3 , exhausting with AcOEt , washing the ext. and evapp. it *in vacuo*, finally with the addn. of H_2O . From the tannin so obtained fractions of high and low rotation could likewise be obtained by I.'s method. The former, apparently much purer fraction (A), showed about the same sp. rotation at all concns. between 0.5 and 5%, while the fraction of low rotation could be polarized only in 0.5% aq. soln.; in org. solvents it dissolved clear only in $\text{C}_6\text{H}_5\text{N}$, in which it unexpectedly showed the same sp. rotation (40°) as A; in both cases the rotation was independent of the concn. A prepn. with low rotation

(19° in H_2O) was then dissolved in $AcOEt$, filtered and worked up; it now had a rotation of 60° in H_2O (0.5% soln.) and still the same rotation (40°) in C_6H_5N . In other org. solvents all preps. (both of high and low rotation in H_2O) showed sp. rotations almost independent of the concn. and approx. the same for all preps. in any one solvent, viz., $HCONH_2$ 13, Me_2CO 14, $EtOH$ 18, $AcOH$ 25, C_6H_5N 40°. These results led to the conclusion that the peculiar behavior of the aq. solns. is due to colloidal phenomena and that it is an admixture insignificant in amt. which influences the rotation of the chief constituent of the tannin. Attempts were accordingly made so to prep. the tannin that most of the impurity was removed beforehand. The first improvement was effected by extg. the galls at room temp. instead of with heat; the product so obtained already showed $[\alpha]_D^{20}$ 90° in 3% aq. soln. and the sp. rotation was hardly affected by the concn. Expts. with inorg. adsorbents (kaolin, Al_2O_3) and org. precipitants (starch, albumin, casein, gelatin) failed further to raise the rotation. When, however, the 90° product was dried at 100° *in vacuo* and extd. with cold dry $AcOEt$ there was obtained from the $AcOEt$ a lighter product with $[\alpha]_D^{20}$ 116° (1% aq. soln.), and repetition of the process twice gave a product with a const. rotation of 138° (1.5% aq. soln.). F. and S. believe that the tannin is on the whole homogeneous and, when pure, dissolves in H_2O in such a way that the mols. are sepd. from each other and are thus present in the finest conceivable state of subdivision, but the soln. cannot be considered as mol. dispersed in the ordinary sense, for it has the familiar colloidal properties owing to the size of the tannin mol. itself (1700?) and possibly owing to its association with the surrounding H_2O . The magnitude of the rotation of one and the same substance in the same solvent depends primarily on the no. of the particles, decreasing when the no. of these particles is diminished. Such a diminution in the no. of the particles, i. e., the association of individual tannin mols., is believed to be produced by the impurity mentioned above. The natural tannin of high rotating power now available is to be thoroughly studied and compared with the synthetic products.

C. A. R.

Tannins and similar compounds. XII. The tannin of native oak. KARL FREUDENBERG AND ERICH VOLLBRECHT. *Ann.* 429, 284-317 (1922); cf. preceding abstr.—20 kg. young sprouts of the *Quercus pedunculata*, extd. 10 min. with 50 l. boiling H_2O and then twice with luke-warm water, were completely freed of tannins (no ppt. with $Pb(OAc)_2$). The combined filtrates were pptd. with aq. $Pb(OAc)_2$, giving 2.5 to 3 kg. Pb paste, contg. about 300 g. tannins. The Pb salt was decompd. with H_2SO_4 and again pptd. with $Pb(OAc)_2$, the salt again decompd., a slight excess of acid added and the ellagic acid filtered. This soln. was then extd. with H_2O for 100 hrs. The Et_2O removed ellagic acid, quercetin pentosides and hexosides, fats, etc. The aq. soln. was then extd. for 48 hrs. under diminished pressure with $AcOEt$, which removed quercetin compds. On hydrolysis of the $AcOEt$ ext. a mixt. of sugars was obtained, containing 19% pentose with glucose. In a mixt. of quercetin, its glucosides and ellagic acid, the glucosides may be removed with warm H_2O , while quercetin may be extd. with cold $(CH_3OH)_2$, $HCONH_2$, or warm $MeCN$ and identified as the pentaacetate. Colloidal quercussic acid (see below) has no influence upon the optical activity of quercitrin in alc. but markedly increases that in H_2O . The extd. aq. soln. of the tannin is then exactly neutralized with $Ba(OH)_2$, pptd. with $Pb(OAc)_2$ in small portions until the ppt. is a pure yellow, filtered, and the clear soln. treated with $Pb(OAc)_2$ until about 0.1 of the tannin is pptd. Without filtering this is treated with H_2S until all the Pb is removed. This decreases the yield but improves the product. The filtered soln. is then concd. to dryness, dried *in vacuo*, extd. with alc. and further purified by treatment with a little H_2SO_4 and H_2O . The tannin forms a reddish yellow amorphous material, with 1% ash, sol. in H_2O with a strongly acid reaction (1 g. required 22.5 cc. 0.1 N alkali). The sp. rotation varied between -30° to -50° in H_2O and -20° to -40° in $MeOH$. It is MeO -

free. Hydrolysis with *N* NaOH gave 18-24% ellagic acid and 3-7% bound sugar. No fractionation of this material was effected by extn. with AcOMe or AcOEt or by fractional pptn. with Pb(OAc)₂. Repeated pptn. of an alc. soln. with Et₂O gave fractions varying in acidity from 8 to 25 cc. 0.1 *N* alkali per g., although the other properties were very similar. Decompn. of the tannin with *N* NaOH leads to the splitting off of the ellagic acid and the formation of an optically active compd. of glucose with "quercussic acid." This proves that the glucose is not bound to the ellagic acid. The new acid is obtained by the action of tannase upon the tannin; it is a reddish yellow amorphous substance optically inactive, 1 g. of which requires 26 cc. 0.1 *N* alkali for neutralization. *Aspergillus niger* does not attack the new acid and its action may be used to facilitate its prepn., since tannase acts very slowly. This action may take place upon the extd. shoots or in H₂O contg. the shoots themselves. The time required is from 2 to 3 months, and the yield is about 5% of the wt. of the shoots. The tannin from *Quercus sessiliflora* appears to have the same properties as that from *Q. pedunculata*. Tannins prepd. from material gathered later in the season (Nov.) have a lower acidity and lower ellagic acid content.

C. J. WESSER

Cinnamylformic acids. GUSTAV HELLER, HILDE LAUTH AND ARNOLD BUCHWALDT. *Ber.* 55B, 2679(1922).—It had escaped the attention of H., L. and B. (C. A. 16, 2682) that Cusa had been able to prep. *m*- and *p*-nitrocinnamylformic acids (designated by him as nitrobenzalpyruvic acids) by condensation in alk. soln. (C. A. 14, 173).

C. A. R.

Catalytic hydrogenation of liquids under the influence of common metals. VII. Phenols. ANDRÉ BROCHET. *Bull. soc. chim.* 31, 1270-80(1922); cf. C. A. 8, 3180; 9, 1912, 1746.—Aromatic ethylenic linkings hydrogenate with greater difficulty than aliphatic, but the presence of a phenol hydroxyl aids the hydrogenation. Polyphenols are more difficult to hydrogenate than PhOH. Phenolic ethers hydrogenate with difficulty. Pure crystd. PhOH with active Ni as catalyst, at 100-50° and 10-15 atm. gave good yields of pure cyclohexanol (b. 160.5°) free from cyclohexane and cyclohexanone. Crude carbohic acid and "95% straw-colored acid" gave poor results. Pure *o*-methylcyclohexanol (b. 163-4°) was obtained in almost theoretical yield by hydrogenating *o*-cresol at 160-70° and 25 atm. *m*-Cresol and *p*-cresol gave *m*-methylcyclohexanol (b. 170-1°) and *p*-methylcyclohexanol (170-1°), resp., under the same conditions. Data on the effect of the temp. and pressure factors on the hydrogenation of phenol and the cresols are included. **VIII. Naphthols.** A. BROCHET AND R. CORNUBERT. *Ibid* 1290-3.—The methods of B. make possible the prepn. of the 4 tetrahydronaphthols. Active Ni, prepd. by calcining 25 g. basic carbonate and reducing the oxide formed in a current of H₂ at 300° for 48 hrs., was introduced into 200 g. melted α -naphthol, and the naphthol hydrogenated at 130°, and 15 kg. pressure per cc., 95% of the theoretical amt. of H was absorbed. The product was dissolved in alc., the Ni filtered off, the alc. distd. off, and the residue washed with dil. NaOH and extd. with Et₂O. The caustic soln. was treated with HCl and extd. with Et₂O, giving 30 g. (15% total yield) *ar*-tetrahydro- α -naphthol, m. 68° (cor.). The first Et₂O ext. gave on distn. 139 g. (85% total yield) *ac*-tetrahydro- α -naphthol, b₁₇ 139-40° (cor.), d₁₇ 1.0896, n_D²⁰ 1.5671, stable, shows abnormal dispersion, has an absorption band in the red; phenylurethan deriv. needles m. 121°. 3-Naphthol was hydrogenated in the same manner at 150°, the theoretical amt. of H being absorbed. Further hydrogenation even at 200° and 16 atm. was impossible. There were obtained 75 parts *ac*-tetrahydro- β -naphthol, very viscous liquid, turning brown in the air, b₂₀ 144.5-6.5° (cor.), b₃₃ 174.6-3.5° (cor.), d₁₇ 1.0715, n_D²⁰ 1.5523, has a normal spectrum (phenylurethan deriv., needles m. 99°), and 25 parts *ar*-tetrahydro- β -naphthol, oil, shows a tendency to superfusion, m. 57.5°. The influence of the phenol hydroxyl in the ease of hydrogenation is substantiated by the high percentage of alicyclic compds.

A. C. PURDY

The synthesis of the phosphoric acid esters. I. SHIGERU KOMATSU AND SHIN-ICHIRO KUMAMOTO. *Mem. Coll. Sci. Kyoto Imp. Univ.* **6**, 45–8(1922).—The prepn. of new hexahydrophenol (A) esters is described. By a method used by Posternak for the inosyl esters (cf. *C. A.* **13**, 2547; **15**, 1891) H_4PO_4 , A and P_2O_5 let stand at room temp. for some days, dild. with H_2O , the lower layer sepd. from the brown oil above, neutralized with $Ba(OH)_2$, the excess $Ba(OH)_2$ pptd. with CO_2 , filtered, evapd. to dryness and recrystd. from H_2O , gave the compound $C_6H_{11}BaPO_4$ (B), white crystals. The oil layer, dissolved in Et_2O , treated with $Ba(OH)_2$, the excess $Ba(OH)_2$ removed by CO_2 , evapd. to dryness and the residue extd. with Et_2O , gave a residue of B. The Et_2O ext. was divided into 2 parts. (1) Treatment with dry NH_3 , and the ppt. treated with $AgNO_3$ gave the compound $C_6H_{11}Ag_3PO_4$. (2) Evapn. almost to dryness and letting stand 3 weeks, in a desiccator, gave the compound $C_6H_{11}H_3PO_4$ (C), colorless crystals, m. $77-80^\circ$, sol. in H_2O , Et_2O and $EtOH$, decompd. by heat into H_3PO_4 and tetrahydrobenzene. Barium salt, sol. in H_2O , decompd. by heat like C. Ammonium salt, sol. in H_2O . Silver salt, insol. in H_2O . 50 g. A and 35 g. $POCl_3$ let stand several weeks, dild. with H_2O and then aq. NaOH, the oily residue steam-distd. and the distillate (b. $230-80^\circ$) fractionated at 6–7 mm. pressure, gave 2 fractions; (1) a colorless liquid, b_{6-7} $100-25^\circ$ (yield 2.5 g.), d_4^{25} 0.9903, n_D^{25} 1.5028, contg. 77.52% C and 9.95% H; (2) a light yellow-orange liquid, b_{6-7} $126-7^\circ$ (yield 2.5 g.), d_4^{25} 0.9938, n_D^{25} 1.5026, contg. 78.75% C, 9.23% H, probably the dihexahydrophenyl ether obtained by Ipatiev and Filipov (*C. A.* **3**, 1014).

C. C. DAVIS

Action of sulfur and of a few sulfur compounds on terpenes. P. P. BUDNIKOFF AND E. A. SCHILOW. *Ber.* **55B**, 3848–53(1922).—Russian turpentine b. $170-5^\circ$ was used. On boiling with S a homogeneous, tough, reddish brown liquid was obtained which on distn. yielded S-contg. fractions. The S content of these fractions is proportional to the increase in b. p. of the fractions. About 50% of the turpentine remains as a residue, which ppts. with acetone solns. of Hg, Au, $PtCl_4$, $Pb(OAc)_2$, AsI_3 , etc. The $AuCl_3$ compd. can be used for ceramic purposes. *Methylterpenesulfonium iodide*, $C_{10}H_{16}S.MeI$ (A) (3% yield from the S fraction by treatment with MeI), m. 121° , sol. in abs. $EtOH$, insol. in ether, slowly decompd. by boiling H_2O . The I is ionizable and ppts. with $AgNO_3$. Mol. cond. 115μ (25° ; v. 100). With Ag_2O A gives a strong base, which ppts. heavy metals and displaces NH_3 from NH_4 salts. The base is decompd. by boiling H_2O . A is interesting in the light of Erdmann's ozonide sulfur theory. $C_{10}H_{16}S.CH_2I.HgI_2$ (B), from A by the action of 1 mole HgI_2 (Smile's method), small light yellow prismatic crystals sol. in acetone, insol. in water. H_2S led into an acetone soln. of B gives only a minute ppt. of HgS . $C_{10}H_{16}S.CH_2I.2HgI_2$, from A by the addn. of 2 moles HgI_2 , citron-yellow prisms, decomp. 100° , easily sol. in acetone, with difficulty in $EtOH$, $CHCl_3$ and ether, decompd. by aq. KI. $C_{10}H_{16}S.CH_2I.AsI_3$, from AsI_3 , and A, dark orange crystals, sol. in $EtOH$, acetone and water (the water soln. is colorless and very acid), readily oxidizable; depositing As_2O_3 on exposure to the air. S_2Cl_2 reacts violently on terpenes, the yield of A being greater than with S (6%). Besides S_2Cl_2 the catalytic action of $AlCl_3$, $HgCl_2$, HgI_2 on the reaction terpenes + S was studied, with no special success. There was no advantage in the use of polysulfides in place of S. G. W. P.

Oxidation of sabinene with chromyl chloride. G. G. HENDERSON, J. McG. ROBERTSON AND D. C. BROWN. *J. Chem. Soc.* **121**, 2717–21(1922).—Sabinene (A) resembles other dicyclic terpenes in its reactions with CrO_2Cl_2 . When a 10% soln. in CS_2 is added to A in the same solvent at 0° , a solid additive compd., $C_{10}H_{16}.2CrO_2Cl_2$, is obtained as a gray powder, which is decompd. by H_2O or moist air. The oxidation product was distd. with steam and *sabinemilanaldehyde*, viscous liquid, b. $215-7^\circ$, was isolated through the bisulfite compds. The *semicarbazone* m. $145-6^\circ$. *Sabinenilanic acid*, $C_{10}H_{16}CO_2H$, is obtained by spontaneous oxidation of the aldehyde and also by heating

it with dil. HNO_3 , small prisms, m. $175-6^\circ$. The sodium, calcium and barium salts are readily sol. in H_2O ; the silver salt is almost insol. The ketone proved to be 4-isopropylidenecyclohexanone (C. A. 2, 1008). 4-Isopropylidenecyclohexanol, by reduction of the ketone with Na, viscous liquid, b_{10} 134° ; *p*-nitrobenzoate, small prisms, m. 63° . A small quantity of a 2nd product was isolated, the semicarbazone of which m. 169° (4-isopropyl- Δ^4 -cyclohexenone(?), C. A. 2, 1830).

C. J. WAST

New stearoptene (probably a phenol ether) occurring in some essential oils of the Myrtaceae. A. R. PENFOLD AND F. R. MORRISON. *J. Proc. Roy. Soc. N. S. Wales* 56, 87-9 (1922).—The oils yielding this new constituent in greatest amt. are from *Baeckea crenulata* (5.5%) and *Darwinia grandiflora* (2%); its formula appears to be $\text{C}_{15}\text{H}_{18}\text{O}_4$; primrose-yellow needles, m. $103-4^\circ$, readily sol. in hot EtOH , hot Et_2O , AcMe, xylene, CHCl_3 and C_6H_6 , moderately sol. in EtOAc , sparingly sol. in petr. ether. Apparently this stearoptene contains 2 MeO groups.

W. O. FE.

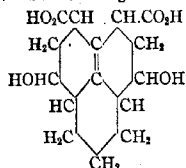
Camphor sol, *p*-diketocamphan and *p*-hydroxycamphor. H. LÖ. *Deut. med. Wochschr.* 48, 377-8 (1922).—Camphor sol, Merck, not yet on the market, is a 3% colloidal soln. of camphor with 10% lecithin. In animal expts. it proved less active than camphor oil or camphor water. Clinical tests have not been made as yet. The hydroxycamphor of Schrötter and the *p*-diketocamphan of Bredt were tested in animal expts. The diketocamphan has α_D 103.42° , and forms white odorless crystals easily sol. in water; it has a marked camphor action on the respiration and on the isolated heart weakened by chloral hydrate, has a pronounced stimulating action on the cerebral cortex of narcotized animals and produces tonic convulsions. Hydroxycamphor also forms odorless crystals easily soluble in H_2O . It has about the same properties as the former compd. but does not elicit convulsions as readily.

S. AMBERG

Condensation products of phenylhydroxylamine with hydroxymethylene compounds and carbinols. IV. Methyleneamphorphenylhydroxylamine. H. RUFF AND W. DIEHL. *Helvetica Chim. Acta* 5, 906-22 (1922); cf. C. A. 16, 1938.—Methyleneamphorphenylhydroxylamine (A) may also be reduced to anilidomethylenecamphor by NaHSO_3 . The action of SOCl_2 upon A in Et_2O gives the *N*-chloride, short yellowish prisms, m. $102-3^\circ$. Since it is possible that a rearrangement may occur in this reaction, methylenecamphor-*p*-chloranilide was prepd. from hydroxymethylenecamphor (B) and *p*- $\text{ClC}_6\text{H}_4\text{NH}_2$, small prisms, m. $167-9^\circ$. A hydrobromide, by addn. of A to satd. AcOH -HBr, yellow needles, m. 121° (decompn.). The HBr is easily split off by warming in EtOH , C_6H_6 or upon soln. in dil. alkali. Br in AcOH gives the dibromide, fine, pale-yellow needles, m. 117° (decompn.). The reaction of A and PhNHNH_2 gave the compd. $\text{C}_{17}\text{H}_{23}\text{N}_2$, identical with that obtained from B and PhNHNH_2 . The same is true of the reaction of A and $\text{H}_2\text{NNHCONH}_2$; the semicarbazide m. $205-6^\circ$ (not $217-8^\circ$, as Wallach gives). The oxidation of an alk. soln. of A with $\text{K}_3\text{Fe}(\text{CN})_6$ gave a compound $\text{C}_{14}\text{H}_{10}\text{O}_4\text{N}_2$, monoclinic prisms, m. $206-8^\circ$ (decompn.). Crystallographic data are given. Tetrabromide, orange-red powder, sintering between $75-125^\circ$. If a CHCl_3 soln. of this compd. is allowed to stand, colorless needles sep., m. $205-8^\circ$, which apparently are a tribromide ($\text{C}_{17}\text{H}_{10}\text{O}_2\text{NBr}_3$); in the air the crystals rapidly turn a brownish red. If a CHCl_3 soln. of the tetrabromide is evapd. to dryness and the deep red resin taken up in EtOH , H_2O ppts. a yellow powder which changes to orange-red upon pptn. from CHCl_3 , decomp. $123-6^\circ$ and analyzes as a dibromide, $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2\text{Br}_2$. The compd. $\text{C}_{14}\text{H}_{10}\text{O}_4\text{N}_2$ dissolves in 75% H_2SO_4 with the formation of a new compound, $\text{C}_{14}\text{H}_{10}\text{O}_4\text{N}_2 \cdot 2\text{H}_2\text{O}$, small microplates, decomp. $190-5^\circ$, easily sol. in NaOH and $\text{Ba}(\text{OH})_2$, from which it is pptd. by acids. Methyl ether, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$, small prisms, m. $226-8^\circ$. Methyleneamphor-*p*-aminophenol methyl ether, fine leaflets, m. $169-72^\circ$. Acetate, leaflets, m. $221-3^\circ$. The properties of these compds. as well as of the parent compd., are so different from those of A and its derivs. that there is no indication of a rearrangement in the condensation of B with PhNHOH .

C. J. WAST

Nature of shellac. Shellolic acid. G. HARRIS AND W. NAGEL. *Ber.* **55B**, 3833-48(1922).—The early work of Tschirch is confirmed. *Pure resin.* The wax- and pigment-free shellac is extd. 10 times with 1-2 l. of ether. If the resin gums during the extns. dissolve in water and reprecipitate with alc. This product is insol. in NH_3 , $\text{Na}_2\text{B}_4\text{O}_7$, and Na_2CO_3 , sol. in dil. caustic alkalis. Yield 79-81%. *Pure resin* can be prepd. from all good grades of comm. shellac. Bleached shellac cannot be utilized. Its compn. is C 65.95-66.57%, H 8.86-9.12%. 0.2 g. in alc. neutralize 1.81-1.98 cc. 0.1 N KOH. *Decomposition of pure resin.* A 15% yield of aleuritic acid (A) was obtained by prolonged hydrolysis of an alk. soln. with steam. A was identified as trihydroxypalmitic acid by its reduction to palmitic acid with HI and P. Ba aleuritate is very slightly sol. in water. A lactonizes and esterifies very easily. *Shellac resin acid mixt.* The filtrate from A is neutralized and extd. with ether and the ether ext. shaken with $\text{Ba}(\text{OH})_2$. The Ba salts so obtained in H_2O soln. are purified after concn. by pptn. with ZnCl_2 . The acids remain in soln. and are obtained by neutralization of the filtrate with NaOH and evapn. to dryness. The residue is extd. with EtOH and the yellowish hygroscopic Na salts are decompd. with dil. H_2SO_4 . The free acids are not hygroscopic. The yield of *resin acid mixture* is 35-8%. The av. of a large no. of analyses showed that the *pure resin* contained: aleuritic acid 30%, ether-insol. resin 1-2%, water-sol. resin acids 4-6%, *resin acid mixt.* 35-38% and residue 10%. The *resin acid mixt.* is very resistant to crystn. and decomp. 50°. The alkali salts are extremely sol. in water and EtOH, the alk. earth salts are only sol. in water, insol. in EtOH, the heavy metal salts Ag, Cu, Pb, Cd, Zn are appreciably sol. in water. *Dimethyl(?)shellolate (B)*, $\text{C}_{17}\text{N}_2\text{O}_8$. The resin acid mixt. is methylated by Fisher's method, giving a light yellow sirup which on rubbing with ether yields B, crystallizable from EtOAc, m. 149°, b_{D}^{20} 284-8° (decompn.), sol. in CHCl_3 , EtOH, C_6H_6 , PhMe, moderately sol. in alc., slightly sol. in ether, insol. in petroleum ether (yield, 8-10% of *pure resin*), mol. wt. (in camphor) 333, 325, $[\alpha]_{\text{D}}^{20}$ 32.61° (MeOH). *Shellolic acid (C)*, from B by sapon. with 0.1 N NaOH, crystals from water, m. 199.5-201°, decomp. 202-3°, fairly sol. in EtOH, hot water, difficultly sol. in Et₂O, EtOAc, C_6H_6 , CHCl_3 , insol. in ligroin, sol. in NaHCO_3 with liberation of CO_2 , acid to litmus, gives the Liebermann cholesterol and the Salkowski-Hesse reaction, does not reduce Fehling soln. but oxidizes alk. KMnO_4 and forms an ozonide, is very sensitive to HCl. *Salts of C:* Amorphous Na and Ba salts were prepd. The Ag, Cu, Pb salts are obtained as ppts. which dissolve on diln. with H_2O . *Hydrazide of C* (1.6 g. from 2 g. B boiled with 30 cc. N_2H_4 for 6 hrs.), insol. in cold EtOH, Et₂O, C_6H_6 , EtOAc and ligroin, moderately sol. in hot water, m. (decompn.) 243-4°. *Diacetylshellolic acid*, obtained by boiling C for 3 hrs. with an excess of Ac_2O , does not cryst. *Diphenylurethan of B*, prepd. by refluxing on a water bath for 6 hrs. 2 g. B with 15 cc. PhNCS, crystals from CHCl_3 , m. 92-4°, sol. in Et₂O, EtOH, EtOAc and C_6H_6 , insol. in petroleum ether. C is a dibasic acid contg. two OH groups. It is undoubtedly unsatd. and the parent hydrocarbon $\text{C}_{15}\text{H}_{22}$ is designated as *shellan*. The following formula is proposed for C. The non-



crystallizable ester fraction obtained in the isolation of B is sepd. by vacuum distn. into an optically inactive distillate and an optically active residue. This research indicates that the shellac mol. is built up of HO acids joined together in lactone couplings, the simplest member of the resin being represented thus:

PbO₂ which does not react with Ph₃C—; Ph₃CNHPh from Ph₃C— and PhNH— or (Ph₃C)₂NPh from Ph₃C— and PhN= might therefore be probable products. The expts. showed that the radical PhNH[•] unites with Ph₃C—, the good yields obtained are due to the slow rate of polymerization of the radical, the slow oxidation of PhNH₂ and the large excess of Ph₃C—. The further course of the PhNH₂ oxidation may oxidize the PhNH— to PhN= or, as appears more likely, the extremely unstable radical may change according to the Wieland rule (cf. C. A. 5, 3286): 2PhNH— → PhN= + PhNH₂. The polymerization of PhN= proceeds then as previously described. PhNHNHPh decomps. when heated in high boiling solvents and for this there are 4 possibilities: (a) PhN= + PhNH₂; (b) 2PhNH— → PhN= + PhNH₂; (c) PhN:NPh + 2H; (d) PhNHNHPh + 2H → 2PhNH₂ (cf. C. A. 7, 2397; 9, 2539). The decompn. of PhNHNHPh in the presence of Ph₃C— substantiates Wieland's view as given above under c and d; almost quant. yields of PhN:NPh and Ph₃CH were obtained; according to a unchanged Ph₃C— and according to b Ph₃CNHPh would be expected. The ease with which Ph₃C— is converted to Ph₃CH is striking (cf. C. A. 5, 2838); in accordance with the Wieland oxidation theory, Ph₃C— is the "acceptor" for the activated H. 50 g. PbO₂ and 50 g. fused Na₂SO₄ were dried by heating 4 hrs. *in vacuo*; 4.8 g. (Ph₃C)₂

was added, the air displaced with dry CO_2 ; then 500 cc. abs. Et_2O and 1.6 g. PhNH_2 was added, the mixt. shaken for 15 hrs., filtered, the $\text{Ph}_3\text{C}-$ pptd. as $(\text{Ph}_3\text{C})_2\text{O}$ by passing air through the soln. and the Et_2O evapd. *in vacuo*; the residual oil became cryst. on adding ligroin; recrystn. gave prisms of *anilinotriphenylmethane*, m. $148-9^\circ$ (cf. *Elbs, Ber.* 17, 703(1884)). In a similar manner, *p*-toluidine gave *p*-toluidinotriphenylmethane, crystals from ligroin, m. 176° (cf. Wittich, *Ber.* 17, 706(1884)); *o*-toluidine similarly gives *o*-toluidinotriphenylmethane, crystals from Et_2O , m. 142° . 1.33 g. PhNH-NHPh and 3.5 g. $\text{Ph}_3\text{C}-$ dissolved in PhMe previously dried over Na were refluxed 5 hrs. in an atm. of CO_2 ; evapn. *in vacuo* at $40-50^\circ$ gave an oil which was dissolved in Et_2O and pptd. with HCl in Et_2O . The pptd. hydrochloride (A) is removed and the filtrate washed with Na_2CO_3 and then with H_2O ; on drying with Na_2SO_4 and evapn. Ph_3CH is obtained by recrystn. of the residue from EtOH ; A was treated with Na_2CO_3 , extd. with Et_2O , and on evapn. gave PhN:NPh . VII. The oxidation of aniline. II. *Ibid.* 3220-7, cf. G. and Strohmenger, *C. A.* 17, 732.—Previous work has shown the probability of the intermediate formation of *N*-phenylquinonediimide (A); two known polymerization products of A are the dimol. *emeraldine* (B) and the trimer (C) obtained by condensation of $\text{NH}_2\text{C}_6\text{H}_4\text{NHPh}$ and A (cf. *C. A.* 4, 324). It is now shown that A by polymerization may yield either B or C depending on the H-ion concn. Oxidation of PhNH_2 salts with PbO_2 (cf. *C. A.* 6, 368; Börnstein, *Ber.* 34, 1268(1901)) gives *dianilino-N*-phenylquinonediimide (E), which is also formed by interaction of A and PhNH_2AcOH ; *azophenine* (F) is formed from PbO_2 and PhNH_2 or from A, AcOH and PhNH_2 . PhNH_2 on oxidation with H_2O_2 in AcOH (cf. Schunck and Marchlewski, *Ber.* 25, 3574(1892)) gives *N*-phenylquinoneimide (G) which condenses with PhNH_2 to form *dianilinoquinoneanil* (H) (cf. Bandrowski, *Monatsh.* 9, 415(1888)). Other oxidation products of PhNH_2 are dianilinoquinone (cf. *C. A.* 4, 3239); dianilinoquinoneimide (cf. Caro, *Z. anorg. Chem.* 1898, 845) and an isomer (cf. *C. A.* 5, 1442) which no doubt are formed by complex reactions involving partial oxidation of A to quinone or quinone imide which condense with PhNH_2 . It is concluded that the varied behavior of PhNH_2 on oxidation is due to the reactivity of A and that very few products arise from the polymerization of $\text{PhN}=\text{}$. Nitrodiphenylamine (I) (cf. Fischer and Hepp, *Ber.* 19, 2994(1886)) was prepd. in 60% yield by adding 50 cc. Et_2O satd. with HCl at 0° to 75 g. dry Ph_2NNO in 325 cc. abs. Et_2O and 65 cc. EtOH , keeping at 0° and stirring; after 15 min. it is allowed to rise to room temp., filtered after 3 hrs. and washed with Et_2O ; 5 cc. of $\text{Et}_2\text{O-HCl}$ are added to the filtrate to obtain after 1 hr. a 2nd crystn.; the crystals, after washing with H_2O , m. 143° . A was prepd. from I (cf. *C. A.* 1, 2606) and was recrystd. from hexane. C was prepd. by adding 5 g. AcOH in Et_2O to 8 g. A in 150 cc. abs. Et_2O , allowing to stand overnight, washing with Na_2CO_3 and then H_2O , filtering, drying with Na_2SO_4 and then evapn.; the violet cryst. residue, recrystd. from xylene and then from C_{10}H_8 , m. 212° ; C was also prepd. by adding $\text{Et}_2\text{O-HCl}$ to A in $\text{Et}_2\text{O-EtOH}$. E was prepd. by adding 50 g. PhNH_2 and 5 cc. AcOH in Et_2O to 9 g. A in 150 cc. cold EtOH ; after 2 hrs. at room temp. the soln. was extd. successively with 3 portions of dil. AcOH , Na_2CO_3 and H_2O ; evapn. of the Et_2O gives a product crystg. slowly after the addn. of MeOH ; recrystd. by boiling in Et_2O with charcoal, filtered, freed from the Et_2O by evapn., and recrystd. from PhH-MeOH , it m. 162° ; E was also prepd. by adding during 3 hrs. a mixt. of 150 g. PhNH_2 , 100 g. AcOH and 300 cc. H_2O to 14 g. A in abs. EtOH ; after standing overnight the soln. is decanted from the sepd. material which is washed with dil. AcOH and H_2O , dissolved in Et_2O , evapd. *in vacuo*, treated with MeOH and recrystd. from PhH-MeOH ; the mother liquors contain F, m. 236° . F was prepd. from 0.2 g. E, 2 g. PhNH_2 and 3 drops AcOH ; after 3 hrs. the mixt. was warmed 10 min. on a water bath, the Et_2O evapd. and the product recrystd. from PhMe . Hydrolysis of E in EtOH with dil. HCl for 2 hrs. gives H; when

the soln. was neutralized with NaOH, extd. with Et₂O and evapd., the residue after extn. with Et₂O gave crystals from AcOH and EtOH, m. 201.5°; E was also obtained by adding AcOH to G and PhNH₂ in Et₂O and recrystg. the product which seps. after 1 hr.

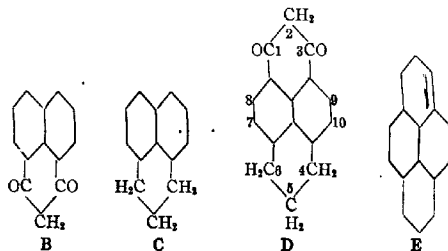
N. A. LANGE

5-Aminoacenaphthene. KARL, FLEISCHER AND KARL, SCHRANZ. *Ber.* 55B, 3253-80(1922).—Attempts to prep. 5-aminoacenaphthene (A) by reduction of the 5-NO₂ compd. (B) with Na₂S₂O₄ gave a 20% yield and not the 70% previously reported (cf. C. A. 4, 3231; 6, 95), the chief product of the reaction being a 50% yield of sodium *N*-acenaphthyl-5-sulfamate (I) (cf. *Compt. rend.* 142, 1052(1906)), which is hydrolyzed to A on heating for a short time with dil. acids; the isomeric SO₃H acids are not hydrolyzed with dil. or concd. acids. The reaction to form I is probably: C₁₂H₇NO₂ + 2Na₂S₂O₄ + 3H₂O = C₁₂H₇NHOH + 4NaHSO₃; C₁₂H₇NHOH + HSO₃Na = H₂O + C₁₂H₇NHSO₃Na. At the same time a 4% yield of 5-aminoacenaphthene-4-sulfonic acid (C) is formed. A, prepd. by reduction of B (cf. C. A. 6, 95) modified by adding 1000 cc. H₂O after removal of the EtOH, then boiling and recrystg. the pptd. A from ligroin, m. 108°; the aq. filtrate was evapd. to 250 cc. when I sepd. and was purified by boiling in H₂O with charcoal, filtering and adding EtOH; crystals, m. 235° (decompn.); I in H₂O with HCl ppts. acenaphthyl-5-sulfamic acid, which m. above 270° and is sol. in EtOH or H₂O and slightly sol. in dil. HCl. To prep. A 200 cc. hot H₂O is added to 40 g. B in 400 cc. boiling EtOH; 100 g. Na₂S₂O₄ is then added and the boiling continued 10-5 min.; after evapn. of the EtOH, 200 cc. H₂O and 200 cc. HCl are added and the soln. is boiled 0.5 hr., dild. with 1000 cc. hot H₂O, treated with charcoal and filtered, and the charcoal washed with hot H₂O and NH₄OH added to ppt. A. The charcoal residue above was boiled with NaOH, filtered and acidified when C sepd. in 4% yield; crystals, from H₂O, darkens at 270° but does not m. 5-Aminoacenaphthene-6(?) -sulfonic acid (D), prepd. in 91% yield by heating for 3 hrs. 20 g. A and 100 cc. 80% H₂SO₄, pptg. with ice and H₂O, dissolving in NH₄OH and reprecip. with acid, crystals, does not m. below 300°, insol. in EtOH, Et₂O, PhH or AcOH. D with diazotized *m*-nitroaniline gives a brown-red azo dye, C₁₂H₇(NH₂)(SO₃Na)(N₂C₆H₄NO₂). D was diazotized and coupled with β-C₁₀H₇OH, giving the azo dye, C₁₂H₅(SO₃Na)N₂C₁₀H₇OH. The following 5-benzylideneamino derivatives of A were prepd. in boiling EtOH soln. by adding the corresponding aldehyde, cooling and recrystg.: benzylidene, from EtOH, m. 67-8°; *o*-nitrobenzylidene, from EtOH, m. 135°; *m*-isomer, from EtOH and then CCl₄, m. 156°; *p*-isomer, from PhH, m. 226°; *o*-chlorobenzylidene, from EtOH, m. 112-4°; *p*-compound, from EtOH, m. 126-8°; *o*-hydroxybenzylidene, from ligroin, m. 92-3°; *p*-isomer, from EtOH, m. 194-6°; *p*-methoxybenzylidene, from EtOH, m. 85-6°; 3',4'-dimethoxy-2'-styrylbenzylidene, from EtOH + CHCl₃, m. 132-4°; α-fural, from EtOH, m. 106-8°. *N,N'*-Di-[acenaphthyl-5]-urea, CO(NHC₁₂H₇)₂, was prepd. by adding COCl₂ in PhH to A, evapg. the PhH, washing with dil. HCl, then with H₂O; dried and recrystd. from PhNO₂ + EtOH it m. 301° (decompn.), is insol. in EtOH, CHCl₃, PhH, ligroin or CCl₄. *N,N'*-Di-[acenaphthyl-5]oxamide, similarly prepd. from A and (COCl)₂ in Et₂O, forms crystals from PhCl, m. 274-5°, insol. in EtOH, CHCl₃ or PhH. *N,N'*-Di-[acenaphthyl-5]-malonamide prepd. from A and CH₂(COCl)₂ in PhH, forms crystals from AcOH, m. 222-3°. *N,N'*-Di-[acenaphthyl-5]-[diethylmalonamide], from A and Et₂C(COCl)₂ in EtOH, forms crystals from EtOH-CHCl₃, m. 218-20°. *N,N'*-Di-[acenaphthyl-5]-succinamide, from A and (CH₂COCl)₂ in Et₂O, forms crystals from PhNO₂-EtOH, m. 288-9°, insol. in EtOH, CHCl₃, CCl₄, PhH, PhCl and H₂O. 5-Dimethylaminoacenaphthene (E) was prepd. by shaking 0.5 hr. a mixt. of 10 g. A, 20 g. AcONa, 25 cc. H₂O and 20 cc. Me₂SO, warming 0.5 hr. at 80°, making ammoniacal, extg. with Et₂O, evapg. the Et₂O ext., treating the residue with 500 cc. 12% KOH and 10 g. PhSO₂Cl, heating until the odor of PhSO₂Cl disappears, extg. with Et₂O, washing with H₂O, evapg. the Et₂O, adding 20 cc. HCl and 250 cc. H₂O

to the residue, filtering, adding NH_4OH , extg. with Et_2O and drying over KOH ; evapn. of the Et_2O gave an oil which solidified after 24 hrs. and was purified by the PhSO_3Cl treatment followed by distn. with steam in which E is volatile; crystals from dil. EtOH , m. $45-6^\circ$, sol. in EtOH , Me_2CO , PhH , PhMe or ligroin; a *picrate*, prepd. in EtOH , m. $172-4^\circ$; a *methiodide*, prepd. from E and MeI at 100° for 2 hrs., forms crystals from EtOH or H_2O , m. 177° ; attempts to prep. the MeBr deriv. were not successful. 5-Diethylaminoacenaphthene, prepd. like E, was further purified by distn., b_n $202-7^\circ$, followed by recrystn. from $\text{EtOH} + \text{H}_2\text{O}$, and then by decompn. of the *picrate* with NH_4OH , m. $41-2^\circ$; it is readily sol. in PhH or ligroin; a *picrate* from PhH or EtOH , m. 186° (decompn.); the *methiodide*, from H_2O , m. $165-7^\circ$ (decompn.), and is decompd. by boiling H_2O . 5-Benzenesulfonylaminoacenaphthene (F), prepd. by shaking for 10 min. a mixt. of A, PhSO_3Cl and 12% KOH , heating to remove PhSO_3Cl , cooling, filtering, washing the ppt. (G) with KOH , adding acid to the filtrate and repptg. the ppt. thus formed from an alk. soln. with acid, forms crystals from EtOH or PhH , m. $198-9^\circ$; the KOH -insol. ppt. G, washed with HCl and then H_2O to remove A, was recrystd. from $\text{Me}_2\text{CO}-\text{EtOH}$, yielding 5-[dibenzenesulfonylamino]acenaphthene, m. 220° , which is converted to F on boiling with EtONa in EtOH ; 5-*p*-toluenesulfonylaminoacenaphthene, from EtOH , m. $194-5^\circ$; 5-[di-*p*-toluenesulfonylamino]acenaphthene, from AcOH , m. $215-7^\circ$. 5-[2',4'-Dinitroanilino]acenaphthene prepd. by boiling for 1.25 hrs. a mixt. of A, $(\text{O}_2\text{N})_2\text{C}_6\text{H}_3\text{Cl}$ and EtOH , forms crystals from AcOH , m. $177-8^\circ$; 5-[2',4',6'-trinitroanilino]acenaphthene, from A and picryl chloride in EtOH , m. 230° (decompn.). A was diazotized and coupled with R salt, giving a red-violet dye; coupled with 1,4- $\text{C}_{10}\text{H}_7(\text{OH})\text{SO}_3\text{Na}$ (H) a red dye was obtained which is decompd. on drying; similarly diazotized D with R salt gave a blue-red dye and with H a rose-bordeaux red dye. N-[Acenaphthyl-5]-glycine, prepd. in 27% yield by heating A, $\text{CH}_2\text{ClCO}_2\text{H}$ and AcONa in H_2O for 0.5 hr., evapg., mixing with solid $(\text{NH}_4)_2\text{CO}_3$ and then boiling with H_2O , cooling, filtering, adding HCl , filtering, adding almost enough NH_4OH to neutralize the filtrate, filtering and repeating the HCl and NH_4OH treatment on the ppt., crystals from PhNO_2 , m. $210-2^\circ$, readily sol. in excess of alkali or acid; attempts to prep. the indigo analog by fusion with NaNH_2 led to decompn.

N. A. LANGE

Synthesis of pyrene. KARL FLEISCHER AND EWALD RETZE. *Ber.* 55B, 3280-90 (1922); cf. C. A. 8, 664; 7, 991.—*peri-Naphthindandione* (B) was prepd. from C_{10}H_8 , $\text{CH}_2(\text{COBr})_2$ (A) and AlCl_3 ; this was reduced to *peri-naphthindan* (C) (*peri-trimethylenenaphthalene*) (cf. C. A. 5, 1769), which was treated with A, giving 1,2,3,4,5,6-hexahydro-1,3-diketopyrene (D); the latter on reduction gave *pyrene* (E). To 23.4 g. C_{10}H_8 and 42 g.



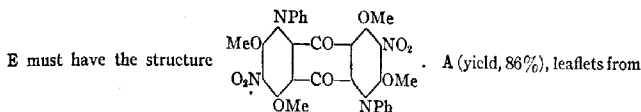
treated with PCl_5 for 2 hrs., sepd. from PhH , dried, and extd. with boiling tetralin EtOH ppts. 1-keto-3,3-dichloro-*peri-naphthindan*, which is sol. in CCl_4 or PhNO_2 and m. about 340° ; attempts to eliminate the Cl with Zn dust and AcOH were not successful. **B** is exceptionally resistant to reducing agents and of the many methods attempted the following only was successful: 5 g. **B**, 3 g. red P and 12 g. HI (d. 2.0) were heated in a sealed tube for 20 hrs. at $160\text{--}80^\circ$; the combined contents of 5 such tubes were transferred to a separatory funnel with Et_2O and H_2O , and the Et_2O ext. was successively washed with H_2O , H_2SO_4 , H_2O , NaOH and then with H_2O until neutral, dried over CaCl_2 , filtered, evapd. and fractionally distd. over Na in *vacuo*; the hexahydro-*peri-trimethylenenaphthalene* mixed with some other reduction products is a light yellow oil, d_4^{25} 0.9624, n_D^{25} 1.5209. The vapors of the mixt. of various reduction products of **B** mixed with CO_2 were dehydrogenated by passing through a 35-cm. tube of freshly reduced Cu heated to 500° ; after cooling, the distillate was united with the Et_2O washings of the Cu and vacuum-distd.; the latter part of the distillate, which solidifies is, **C**, crystals, from dil. EtOH , m. $159\text{--}60^\circ$; that portion of the distillate which does not solidify is unchanged starting material; **C** must be kept in CO_2 ; the red needles of the *picrate*, from EtOH , are oxidized by air and m. $134\text{--}5^\circ$; the 1,3,5-trinitrobenzene addition compound, from EtOH , m. $159\text{--}60^\circ$. 2 g. AlCl_3 was added slowly to 1 g. **C** and 2 g. **A** in 7 cc. CS_2 ; after 0.5 hr. ice was added, the mixt. steam-distd., the solid sepd. from the H_2O , pressed on a porous plate, washed with H_2O , dissolved in warm, dil. NaOH and filtered; HCl pptd. 0.25 g. of **D**, which did not m. below 280° ; **D** without further purification was distd. with Zn dust in an atm. of H_2 ; the distillate solidifies and is **E**; the red needles of the *picrate*, from EtOH , m. $218\text{--}9^\circ$.

N. A. LANGE

New synthesis of dihydrophenanthrene derivatives. E. KIRCHNER. *Nach. kgl. Ges. Wiss. Göttingen, Math.-physik. Klasse* 1921, 154-61.—Benzaloxindole is reduced by H and Pd black to benzylloxindole, fine needles, m. 130° ; when heated with cold satd. Ba(OH)_2 for 4 hrs. at 170° , this yields α -benzyl-*o*-aminophenylacetic acid, which is unstable and was used in the form of the Ba salt. Transformed into the Na salt, diazotized and treated with Cu powder, an acid and a neutral product were obtained. Upon distn. of the 1st in a high vacuum ($170\text{--}270^\circ$), dihydrophenanthrenecarboxylic acid (**A**) was obtained, m. $127\text{--}30^\circ$ (yield, 15%) and also benzylisocoumaranone, yellowish needles, m. $58\text{--}9^\circ$. The neutral part of the original product m. 225° and is sol. in hot NaOH . Prepn. of **A** by Pschorr's synthesis from $o\text{-H}_2\text{NC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CO}_2\text{H})\text{Ph}$ showed that the reaction did not proceed as smoothly as in the case of phenanthrene-itself. *o*-Nitrobenzaloxindole forms fine reddish yellow needles, m. 225° . Hydrogenation of this did not give the expected *o*-aminobenzylloxindole but quindoline, m. above 290° ; acetate, compact needles, m. 185° .

C. J. WEST

Tetranitroanthrachryson. GUSTAV HELLER AND PAUL LINDNER. *Ber.* 55B, 2674-9(1922); cf. C. A. 8, 102.—Tetranitroanthrachryson (**A**), prepd. according to Ger. pat. 76,305 from anthrachryson (**B**) in concd. H_2SO_4 with $\text{HNO}_3\text{--H}_2\text{SO}_4$, is easily sol. in H_2O and is not attacked by alkalis even on long boiling but easily reacts with hot aq. NH_3 ; the reaction, however, is complicated and no homogeneous simple product is formed. The reduction of **A** also does not proceed smoothly and homogeneously and in the complete transformation of the NO_2 into NH_2 groups there begins simultaneously the replacement of an NH_2 group by H ; neither do the products cryst. **A** reacts easily in Na_2CO_3 with org. bases, forming dark dyes, but again no homogeneous products could be isolated. In the belief that the HO groups might be involved in the reaction, tetramethylantrachryson (**C**), prepd. by exhaustive methylation of **B** with alk. Me_2SO_4 , was converted into the tetranitro compound (**D**); this is not attacked by alc. KOH and gives on heating with PhNH_2 and aq. Na_2CO_3 a homogeneous product (**E**) in which two NO_2 groups have been replaced by PhNH . By analogy, these must be in α -positions and



AcOH-petr. ether, turns brown 200°, deflagrates about 285°, is sol. in H₂O, alc. and AcOH with yellow, in Na₂CO₃ with ruby-red color and evolution of CO₂, gives a brick-red salt with an excess of alkali, dyes wool in an AcOH bath bright orange, Cr-mordanted wool in a neutral bath a strong red-brown; unmordanted cotton is unchanged; Cr-mordanted cotton is dyed a bright brown. With SnCl₂-HCl at 70°, A gives *triaminoanthrachryson* (?), black mass with a violet tinge, hardly sol. in the ordinary solvents, sol. in concd. H₂SO₄ with dark green, in NH₄OH and alkalis with blue-violet color, does not change up to 295°, decomps. much higher without melting. With alk. Na₂S₂O₄ on the H₂O bath 4 g. A gives 2.5 g. of the *sodium salt*, C₁₄H₇O₆N₃Na₄, of a *triaminoanthrachryson* different from the preceding compd.; the salt seps. in dark violet needles with a cantharides luster, sol. in alkalis with violet to blue, in concd. H₂SO₄ with green color (red by transmitted light). C, obtained in 80% yield, fine yellow needles from AcOH, m. 238°, sublimes at higher temps., dissolves in concd. H₂SO₄ with violet-red color, is turned red-brown, without dissolving, by alkalis. D (18 g. from 20 g. C), fine yellow needles from AcOH, turns brown 220°, m. 258° (decompn.), sol. in H₂SO₄ with orange color, dyes Cr-mordanted wool a strong red-brown. *Diaminodinitroretetramethoxyanthraquinone* (E) (0.4 g. from 2 g. D), fine dark blue needles from PhMe, gradually decomps. above 300° without melting, sol. in dil. NaOH with dark violet, in NH₄OH with dark blue, in H₂SO₄ with dark green color, dyes wool black-blue. C. A. R.

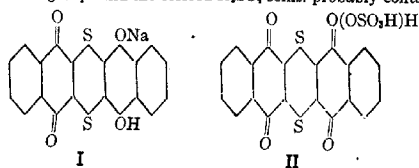
Pyranhydrones. III. Constitution of the methyl-diarylpyrylium compounds.

WILHELM SCHNEIDER AND ALBERT ROSS. *Ber.* 55B, 2775-82 (1922); cf. C. A. 16, 1247.—It had been found that aromatic Me ketones with sulfoacetic acid (A) give the same compds. (B) as obtained by Dilthey from the ketones with Ac₂O and FeCl₃, which he assumed to be the sym. 4-methyl-2,6-diarylpyrylium salts. With weak alkalis, especially NaOAc, they do not form, like the triaryl derivs., the corresponding pseudo bases or pyranols but intensely blue-violet dimol. substances (C) which are formed by the elimination of 1 mol. H₂O from 2 mols. of the pseudo base and which, on account of their quinhydrone-like nature, were designated as "pyranhydrones." As there was no reason for doubting the correctness of the structure assigned by D. to his B, the C were formulated as mol. compds. of 1 mol. each of the oxonium hydroxide base and of the *p*-quinonoid anhydro base or γ -methylene-pyran. S. and R. now undertook to prep. the isomeric 2-methyl-4,6-diarylpyrylium salts and accordingly treated dypnone, BzCH: CPhMe with Ac₂O and A but to their surprise found that the product was identical with that obtained directly from MeCOPh. This can be explained only by assuming that MeCOPh under the influence of the condensing agent (FeCl₃ or A) first forms D which then condenses with AcOH to give B; the B, consequently, do not have the sym. structure hitherto assigned to them but are the 2-methyl-4,6-diaryl compds. The real sym. compd. (E) was now prepd. from an equimol. mixt. of PhCOCH:CHMe and PhCOMe treated with Ac₂O and FeCl₃ and proved to be entirely different from the B; this with NaOAc likewise does not yield the pseudo base but an amorphous dull red substance (F) with faint bluish tinge which is very probably a *pyranhydrazone* having the structure formerly assigned to C, while the latter really have an *o*-quinoid or α -methylene-pyran component. 4-Methyl-2,6-diphenylpyrylium chloride-ferric chloride (E), obtained in 1.5 g. yield from 3 g. PhCOCH:CHMe, 2 g. PhCOMe and 5 g. sublimed FeCl₃ in Ac₂O, m. 205.5°, shows strong light blue fluorescence in dil. solns.; *bromide*, from the FeCl₃ compd. in 2% HCl with concd. KBr, yellow prismatic needles, sol. in H₂O with partial hydrolysis, chars without melting; *iodide*, orange-red needles, gradually decomp.

above 240°; *perchlorate*, fine lemon-yellow needles, m. 273° (decompn.). **F**, best prepd. from the bromide and NaOAc, begins to soften above 70°, darkens from about 95°, m. 155–60°, forms brown dil., brown-red concd. and red very concd. solns. Its pyranhydron nature is indicated by the following observations: A reddish brown CHCl_3 soln. cooled with $\text{Et}_2\text{O} \cdot \text{CO}_2$ distinctly deepens in color towards the red while the same soln. heated a short time to incipient boiling shows a faint but distinct lightening of the color towards light brown. Treated in the cold, light yellow-brown, fluorescent soln. in dild. AcOH with a few drops of HCl, it deposits voluminous, amorphous, brown flocks while a part of the **E** can be recovered from the filtrate as the perchlorate. Heated in a high vacuum up to 130° it sinters and loses markedly in wt., apparently owing to loss of H_2O .

C. A. R.

Transformation of the dithiin ring into the thiophene ring. Dibenzothianthrene-diquinone and dinitrothiophenediquinone. KURT BRASS AND LUDWIG KÖHLER. *Ber.* 55B, 2543–68(1922); cf. *C. A.* 15, 2639.—2,3-Dichloro- α -naphthoquinone (**A**) heated with an excess of concd. aq. Na_2S yields a deep blue-green vat which, when shaken with air, becomes red and deposits a green *monosodium salt* (**I**) of a *dihydrodibenzothianthrene-diquinone* (**B**), from which dil. acids liberate the blue **B**, identical with the blue compd. earlier obtained by incomplete oxidation of the Na_2S melt dild. with H_2O , and which may be considered as an inner quinhydrone. **I** is easily oxidized by alk. H_2O_2 , **B** by dil. HNO_3 , to *dibenzothianthrene-diquinone* (**C**). This method of prep. **C** was soon abandoned, for it was found that an aq. suspension of **A**, protected from the air and shaken with 1.5 mols. Na_2S , likewise yields **I** according to the equation $8\text{A} + 12\text{Na}_2\text{S} + 3\text{H}_2\text{O} = 4\text{I} + 2\text{NaSH} + \text{Na}_2\text{S}_2\text{O}_3 + 16\text{NaCl}$. The dithiin or biophene ring in **C** is remarkably unstable; **C** changes easily into *dinaphthothiophenediquinone* (**D**), either on heating alone above its m. p. or with concd. H_2SO_4 or on long boiling in PhNO_2 . The *dibenso-thianthrene* corresponding to **C** cannot be obtained from **C** by the usual methods; Zn dust distn. cannot be used on account of the instability of the **C** at high temps. and heating some hrs. at 170° with HI and yellow P gives C_{10}H_8 and H_2S . In cold concd. H_2SO_4 , **C** dissolves only slightly, with red color; in fuming acid (15% SO_3) it forms a green soln. and is reprecipitated unchanged by H_2O ; the colors of the solns. are to be attributed to additive thionium or oxonium sulfates. **B** also dissolves in cold concd. H_2SO_4 with brown-red color and is reprecipitated by H_2O . The salt formation is apparently conditioned by the presence of the keto groups and the colored H_2SO_4 solns. probably contain oxonium sul-



fates of the type **II**. As the result of the adjacent keto or acyl and HO groups, the S atoms of **C** and of the acyl derivs. of its di- and tetrahydro compds. seem to have completely lost their basic character. Reduction of **C** in either acid or alk. soln. gives **B** first and then the completely reduced, colorless, unstable *tetrahydro compound* (**E**). **B**, when dry, is characterized by its remarkable stability but when moist or in soln. it easily regenerates **C** with atm. O. Of its two HO groups, only 1 is capable of salt formation but both are easily acylated in $\text{C}_6\text{H}_5\text{N}$, forming well crystd. compds. sol. with red color. **E** oxidizes very easily to **B** (it can be recrystd. from alc. only in a H_2S atm.); it can be liberated from its yellow alk. vats by weak acids (CO_2 , H_2S). Its Ac derivs. are likewise colorless; the diacetate is easily obtained by reduction with Zn dust and AcOH of the corresponding quinone, which it easily regenerates with atm. O from the diacetate in

soln.; in dry state it is quite stable. Further acetylation gives the tetraacetate (F), which, like the tetrabenzoate (G) (prepd. by benzoylating the $\text{Na}_2\text{S}_2\text{O}_4$ vat), crystals well and is difficultly hydrolyzed. On oxidation with cold concd. HNO_3 C yields but one product, the monosulfoxide (H), also obtained slowly by rubbing with somewhat more dil. acid; H is reduced back to C by HBr ; HCl reduces it more slowly; gentle warming with Zn dust and AcOH or treatment with HI-AcOH in the cold converts it into B, C itself not being formed as an intermediate product in this process. H shows a great tendency to split off the S carrying the O; on dry heating it decomps. with liberation of SO_2 and H_2S and on boiling in AcOH or heating in PhNO_2 it evolves H_2S . It can therefore not be recrystd.; the AcOH soln., to be sure, deposits a well crystd. yellow substance (J), which, however, is not H. The yellow soln. of H in cold concd. HNO_3 vigorously evolves NO on gentle warming and on treatment with H_2O deposits J, while the filtrate contains exactly 0.5 of the S in the original H as H_2SO_4 . J is therefore D. D is very stable, sublimes, can be converted into a vat, dissolves unchanged in cold concd. H_2SO_4 with yellow color and shows the same reduction stages as C, giving on gentle reduction with Zn dust and AcOH a green dihydro compound (K) analogous to B, which forms a red insol. alkali salt (apparently of the mono series) and a blue monoacetate (L) and a red diacetate (M); the intensely red AcOH soln. of the latter is easily reduced by Zn dust to the colorless soln. of K. The yellow Na_2S vat of C with H_2S gives the yellow green tetrahydro compound (N) of D, also obtained from D in AcOH with Zn dust or HI; its yellow alk. soln. is very unstable in the air and quickly deposits the red salt of K. The tetraacetate and tetrabenzoate are faintly yellow. The A is obtained in 10 g. yield from 10 g. of 96% α -naphthoquinone in 90 cc. AcOH and 4 g. I treated 1.5 hrs. with Cl; the mother liquors with 10 g. more of the quinone and only 0.5 g. more of I yield 12 g. more of A on similar chlorination and the mother liquors from this second crop can be used for a third chlorination with equally good results. The A so obtained is light yellow and m. $189-90^\circ$. C (*di- α -naphthoquinonodithiin*), dark red-brown needles (red-violet under the microscope) from PhNO_2 , mol. wt. in boiling PhNO_2 , 371, turns brown 280° , m. 302° (decompn.), unchanged by HCl , NaOH or NaHSO_3 , is completely decompd. in alk. suspension by H_2O_2 , does not react with Br in C_6H_6 or AcOH . B (α -naphthoquinone- α -naphthohydroquinonodithiin), deep blue needles from PhNO_2 , oxidizes to C on heating in a m.-p. tube and m. at the m. p. (302°) of C; diacetate, dark olive-green spindles (yellow-green with red reflex in the transmitted light of the microscope) from AcOH , m. $265-8^\circ$, sol. in cold concd. H_2SO_4 with dirty brown color, by which, as well as by hot H_3PO_4 and alc. KOH , it is hydrolyzed to B, sol. in cold concd. HNO_3 (not without change) with yellow color; dibenzoate, red rodlets or leaflets (green with red shimmer under the microscope) from C_6H_6 , AcOH or $\text{C}_6\text{H}_5\text{N}$, m. 290° , easily hydrolyzed by alc. KOH . E (*1,4,1,4'-tetrahydroxydibenzothianthrene, bis- α -naphthohydroquinonodithiin*), needles whose colorless solns. (especially that in alc.) rapidly turn blue in the air, gives, when shaken in its hot $\text{Na}_2\text{S}_2\text{O}_4$ vat with Me_2SO , a colorless methyl ether, hair-like needles from AcOH ; 1,4-diacetate, hair-like needles from AcOH , m. around 262° (previously decomp.), does not at first dissolve in cold concd. H_2SO_4 but after a time goes into soln. with brown color, simultaneously oxidizing and hydrolyzing; tetraacetate (F), needles from PhNO_2 , m. $300-40^\circ$, does not react with Br in AcOH or C_6H_6 , is not attacked by dil. boiling alkali but is hydrolyzed by alc. KOH or boiling H_3PO_4 ; tetrabenzoate (G), rhombic tables from $\text{C}_6\text{H}_5\text{N}$ or PhNO_2 , m. around 360° . H (*di- α -naphthoquinonodithiin sulfoxide*), yellow hygroscopic needles, m. around 270° . D (*bis- α -naphthoquinonodithiophene*), yellow needles from AcOH or CCl_4 , m. 278° , mol. wt. in boiling PhNO_2 , 361.7. K (α -naphthoquinone- α -naphthohydroquinonodithiophene), blue-green needles from PhNO_2 , m. around 265° ; monoacetate (L), blue rodlets or tables (blue-green in the transmitted light of the microscope) from $\text{C}_6\text{H}_5\text{N}$, m. around 290° ; 1,4-diacetate (M),

light red needles from AcOH, m. 254°. *N* (1,4,1',4'-tetrahydroxydinaphthothiophene, bis- α -naphthohydroquinolothiophene), light green needles; tetraacetate, light yellow rectangular or honey comb-like plates from AcOH, m. about 271° (decompn.); tetrabenzoate, light yellow needles from C₆H₆N, m. about 330° (decompn.). C. A. R.

Synthesis of pyrrolidine; reduction of pyrrole by catalytic hydrogenation. N. J. PUTOCHIN. *Ber.* 55B, 2742-8(1922).—The catalytic reduction of pyrrole (A) according to Padoa (*Gazz. chim. ital.* 36, II, 317(1906)) did not prove very satisfactory, as regards the yield for the prepn. of pyrrolidine (B). The A was made synthetically from milk sugar; the catalyst, Ni, was prepd. by reducing the oxide at 350°; the hydrogenation was carried out at 200°; the products were freed from unchanged A by conversion into the HCl salts, then set free with alkali, dried with KOH and fractionated. NH₃ was evolved during the hydrogenation. In the products were detected, besides B, NH₄Et, MeNHPr, BuNH₂, AmNH₂, EtNHPr and a base C₈H₁₃N (C), apparently γ -methylpiperidine. These results show that the ring in A can open at different points simultaneously; the formation of AmNH₂ and AmNH₄Et is most simply explained by assuming that there is first a condensation of 2 mols. A to a piperidine; the precursor of the latter must be a methylated A or B. C, from the fraction of the hydrogenation products b. chiefly 104-5°, yields a chloroplatinate sepg. from H₂O in light yellow radiating spherocrystals. From the fraction b. above 145° is obtained a base C₈H₁₃N or C₁₀H₁₅N (perhaps hexahydroindoline or possibly α -butylpyrrolidine), whose picrate, long green needles from aq. alc., m. 118°. The Gabriel method (*Ber.* 24, 3231(1891)) proved to be the best for prepg. B. It was improved in some respects; by boiling the NaOPh and ClCH₂CH₂CH₂CN 3 instead of 1 hr., the yield of PhO(CH₂)₃CN was increased to 71% and, after reduction to the amine, by distg. the alc. off on the H₂O bath with the aid of a small dephlegmator instead of with steam, the yield of amine was increased 10%. As a by-product in the reduction to the amine was obtained bis- γ -phenoxybutylamine, plates from alc., m. 162-3°, insol. in HCl; γ -phenoxybutyric acid, fine somewhat yellowish scales from ligroin, m. 59.5°, was also detected. Trimethylene chlorobromide, b. 139-42°, the real starting point for the Gabriel synthesis of B, was obtained in 87.2% yield, instead of 50%, by a modification of the Dalle method (*Rec. trav. chim.* 21, 123(1902)). C. A. R.

Action of formaldehyde on pyrrolidine and piperidine. N. J. PUTOCHIN. *Ber.* 55B, 2749-53(1922).—When equimol. amts. of pyrrolidine (A) and HCHO (as trihydroxymethylene) are heated 6 hrs. in sealed tubes at 145-50°, then dried with fused KOH and fractionated *in vacuo*, there are obtained, besides a dark resinous residue, 2 strongly alk. fractions: (1) *Pyrrolidinomethyl alcohol* (B), yellowish sirup, b₃₀ 55-6°, reconverted into its components by dil. HCl even at room temp.; and (2) *N,N'*-dipyrrolidinomethane, yellow liquid with a peculiar, overpowering nicotine odor, b₃₀ 94-5°, mol. wt. (V. Meyer method) 143-65, has a strong tendency to resinify. The dark residue remaining when the above 2 compds. are distd. yields on dry distn. A and a yellow mobile liquid, b. about 140°, which is apparently isomeric with B. Piperidine, treated like A, gives CO₂, a liquid b₃₀ 33-5° which is apparently a mixt. of *N*- and α -methylpiperidines, and *N,N'*-methylenedipiperidine, b₂₀ 120-2°, mol. wt. in freezing C₆H₆ 159-60, d₄²⁰ 0.9371, d₁₁¹⁵ 0.9344, d₁₅¹⁵ 0.9335, n_D¹⁶ 1.4883. C. A. R.

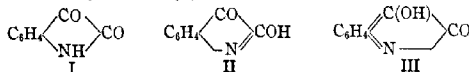
The reaction between acetylene and aniline at high temperatures. RIKO MAJIMA, TADASHI UNNO AND KASHICHI ONO. *Ber.* 55B, 3854-9(1922).—A study of the conditions for obtaining indole by the action of C₂H₂ on PhNH₂ at higher temps. The following catalysts were tried: SiO₂, Fe₂O₃, Cr₂O₃, ThO₂, NiO, CoO, MnO₂, MoO₃, WO₃, V₂O₅, Ta₂O₅, Ni, Fe, Co, Pt, Pd, Os, and Cu. Ni was the best catalyst, but lost its activity very rapidly. *Prepn. of indole*: 1 kg. PhNH₂ was dropped at the rate of 360 cc. per hr. into an Fe tube of 52 mm. diameter, heated at 700° over a length of 75

cm. (The tube itself served as catalyst.) Simultaneously a mixt. of 62 l. C_2H_4 and 27 l. CO_2 was passed through the reaction chamber. The fraction of the tar b. 175–200° was returned to the app. The final yields were: Indole (crude) 65 g. (34%), C_8H_6 22 g., unchanged $PhNH_2$ 812 g., carbazole 9 g., β - $C_{10}H_7NH_2$ 1 g. G. W. PUCHER

Syntheses in the indole series. RIKO MAJIMA. I. A new synthesis of racemic tryptophan. MUNIO KOTAKI. Ber. 55B, 3859–65 (1922).—The synthesis is based upon the following series of reactions: β -indolaldehyde (A) + hydantoin $\xrightarrow{-H_2O}$ β -indolalhy-dantoin (B) $\xrightarrow{+H_2}$ ω -hydantylskatole (C) \rightarrow *dl*-tryptophan (D). To prep. A, 5.9 g. indole in 7–8 cc. anisole were added with vigorous agitation to a Grignard reagent prepd. from 2.4 g. Mg ribbon, 10 cc. anisole (trace of I) and 16 g. (2 mols.) EtI . C_2H_4 was copiously evolved. Then 20 cc. HCO_2Et (5 mol. to 1 mol. indole) were added with cooling. 2.2 g. A, m. 193–5°, and 1.4 g. unchanged indole were isolated. 3.5 g. A, 2.9 g. hydantoin, and 5.8 g. fused NaOAc were heated with 12 cc. Ac_2O for 30 min. at 106–8°. 4.1 g. crude condensation product, m. 280–90°, gave 2.7 g. pure B, m. 320°, decomps. 325°, insol. in ether, $CHCl_3$, H_2O , difficultly sol. in $EtOH$, and C_2H_5OH . *N*-Acetylindolaldehyde and an unidentified compd., m. 198–300°, were also isolated. 8.4 g. B in 450 cc. 2% NaOH was reduced with 350 g. 5% Na-Hg. On neutralizing 6.7 g. crude product was isolated which on crystn. from H_2O gave 5.75 g. pure C (68% yield), m. 220–1°, sol. in $AcOH$ and acetone, pptd. by 10% H_2SO_4 , gives a red-violet color with glyoxylic acid and concd. H_2SO_4 , differs from tryptophan by not coloring with Br water. 2.8 g. pure D (53% yield), crystals from 50% alc., was obtained by heating 5.5 g. C for 6.5 hrs. at 108° with 50 g. $Ba(OH)_2$ and 95 cc. H_2O . D colors at 250° and m. 283–5°. An unidentified compd. contg. 1 mol. H_2O more than C and m. 207° was also isolated by the hydrolysis of C.

G. W. PUCHER

New isomerisms in the isatin series. V. GUSTAV HELLER. Ber. 55B, 2681–97 (1922); cf. C. A. 15, 87.—It had already been shown that besides the lactam form (I) of isatin and its derivs., the lactim (II) and isatol (III) forms also are capable of existence



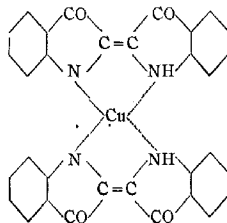
in some cases, and a 4th form of 5,7-dimethylisatin (A), of unknown structure, characterized by its high m. p. and insol. in alkali, has been discovered. These relationships are further complicated by the existence of derivs. of bimol. isatins, the so-called isatoids (C. A. 16, 3653), thus far known only in the form of their *O*-alkyl ethers, the simplest of which, the Me ether, exists in 3 interconvertible isomers. Other substituted isatins have now been studied with respect to their behavior in the isomerization reactions. The Ag salt of 5,7-dibromoisatin (B) treated in C_6H_6 with $BzCl$ gives only a small amt. of the alkali-insol. isomer (C), the chief product being *N*-benzoyl-5,7-dibromoisatinic acid (D), sol. in NaOAc and converted into *N*-benzoyldibromoisatin (E) by Ac_2O . With $AcCl$ under the same conditions is obtained *N*-acetyldibromoisatin (F), whose ring is opened by alkalis only on heating and which cannot be obtained by acetylation of B. The lactim methyl ether (G) of B is obtained in the usual way from the Ag salt and MeI; unlike the *O*-alkyl ethers of isatin and 5-bromoisatin, it is very stable to light, changing but slightly even in the strongest sunlight; it recrysts. unchanged after long heating with Ac_2O ; with $PhNHNH_2$ in C_6H_6 it forms the α -phenylhydrazone of B, the existence for a few sec. of an intermediate colorless addn. product being observable. The alkali salts of B are far more stable than those of isatin; they can be sepd. almost quant. even in the presence of H_2O and the rupture of the ring occurs much more slowly than in isatin. A colorless product, apparently a labile addn. compd., is formed even in 50% alc. In

the case of 4-chloro-5-bromoisatin (H) the Ag salt in C_6H_6 with BzCl gives chiefly *N*-benzoylchlorobromoisatin, together with a very small amt. of a dark, non-crystallizable substance sol. in alkalies and probably belonging to the 4th series of isatin isomers. 5,7-Dichloroisatin (J) gives chiefly *N*-benzoyldichloroisatinic acid (K), together with a very small amt. of the primary product, *N*-benzoyldichloroisatin (L), easily obtained from K with Ac_2O and reconverted into K by cold alkalies. There is also formed a small amt. of dichloroisatol (M), which gives no indophenin reaction, does not react with $PhNHNH_2$ and dissolves with crimson color in dil. NaOH in which it apparently rearranges more rapidly than the non-halogenated isatol, mineral acids pptg. J from the soln. In org. solvents, also, M is unstable; from AcOH it recryst. in a new isomeric form (N), provisionally designated as 5,7-dichloroisatin IV. The Ag salt of J with $AcCl$ gives *N*-acetyldichloroisatinic acid (O), which does not condense smoothly when heated with Ac_2O but decomps. with formation of J. The *O*-methyl ether (P) of J is formed normally from the Ag salt with MeI; it is very stable towards light and is converted by Ac_2O with relative ease into an isatoid (Q), which on heating with $AcOH$ and HBr decomps. into J; in the alc. soln. of P there is transiently formed a colorless addn. product with $PhNHNH_2$. A repetition of the earlier work on A has confirmed the results then obtained as far as the isomers are concerned. Its *O*-methyl ether (R) was obtained from the Ag salt in C_6H_6 with MeI below 70° ; it is very stable towards light but is converted into an isatoid (S) not only by Ac_2O but also on mere heating with PhMe in concd. soln. and then with C_6H_6 in a sealed tube; S is the compd. (obtained at 100°) formerly described as R. Exposed with dil. alkali to daylight S becomes yellow after some days and there are formed yellow needles of what is probably anhydro- α -dimethylisatindimethylanthranilide (T). $Me_2C_6H_2 \begin{array}{c} \diagup CO : N \\ \diagdown N - CO \end{array} C_6H_2Me_2$. 7-Methylisatin (U)

forms no salt of normal compn. in alc. with $AgOAc$, and the product regenerates only U when heated in C_6H_6 with BzCl or $AcCl$. Com. B, purified through the Na salt, is orange-colored, m. $248-9^\circ$, and forms a difficultly sol. $NaHSO_4$ compd. *N*-Silver salt (20 g. from 11.25 g. B), gray-violet ppt., is sol. in C_6H_5N with reddish violet color. D (2.6 g. from 8.25 g. of the above Ag salt), needles from $AcOEt$ -ligroin, m. $207-8^\circ$ (gas evolution). C (0.4 g. from 9.6 g. of the crude D freed from D with $NaOAc$ and from B with dil. NaOH), fine brick-red needles from PhMe, m. above 300° , insol. in acids and alkalies, cannot be recrystd. unchanged from xylene. E, stout yellow crystals from $AcOEt$ -petr. ether, m. $161-2^\circ$, slowly sol. in cold, more rapidly in hot dil. alkalies, acids pptg. 5,7-dibromoisatinic acid, which is also obtained on boiling an alc. soln. a long time and adding H_2O . F (1.8 g. from 4.1 g. of the Ag salt of B), yellow tables, m. 133° . *N*-Acetyl-5,7-dibromoisatinic acid, needles from $AcOEt$ -petr. ether, m. 204° . G, red crystals from C_6H_6 , m. $164-5^\circ$. α -Phenylhydrazone of B (1 g. from 1 g. G), dark red needles from $AcOH$, m. 218° (gas evolution), gives tetrabromindigo on heating with Zn dust and NaOH. When 0.8 g. of G is heated in ligroin (with $PhNH_2$?—ABSTR.) until the color changes through brown to blue there seps. on cooling 0.8 g. substance yielding 5,7-dibromoisatin- α -anilide, short brownish rodlets with metallic luster, m. 189° , when recrystd. from ligroin, and the anil., light blue feathery needles, m. $174-5^\circ$, when crystd. from alc.; it is decolorized by Zn dust and NaOH and reoxidized by the air and yields blue salts in alc. with $NaOEt$ and with $AgOAc$. Dianil (1 g. from 1 g. of the anilide heated 2 hrs. on the H_2O bath with 2.5 g. $PhNH_2$), deep red needles from C_6H_5EtOH , m. $236-7^\circ$, decompd. by hot HCl but very stable towards alkalies, even Na in alc. only producing the blue *N*-salt; silver salt (0.5 g. from 0.45 g. of the dianil in alc. and 0.2 g. $AgOAc$ in hot H_2O), blue ppt. sol. in C_6H_5N with blue color, insol. in NH_4OH . *N*-Sodium salt of B, dark violet. H, recrystd. from 1:1 $EtOH-Me_2CO$, m. $265-6^\circ$; silver salt, blue-gray, dissolves in cold C_6H_5N with red-violet color; *N*-benzoyl derivative,

stout yellow crystals from ligroin, m. 196°, converted by hot dil. alkalis into *N*-benzoyl-4-chloro-5-bromoindatinic acid, m. 188°. *O*-Methyl ether of **H**, m. 173°, gives with PhNHNH₂ in C₆H₆ the 2-phenylhydrazone of **H**, fine dark red needles from alc., m. 235° (decompn.); anilide, m. 276–7° (decompn.). Silver salt of **J**, violet with a grayish tinge, dissolves in C₆H₅N with intense bluish red color. **O**, faintly flesh-colored prisms from AcOH, m. 204° (decompn.). **M** (1.5 g. from 16.5 g. of the above Ag salt), yellow, m. 204° (slight gas evolution), sol. in concd. H₂SO₄ with faint reddish color. **N**, red crystals from AcOH, m. 318°, insol. in alkalis, is not attacked by CH₃N₂, dissolves in hot alc. PhNHNH₂, and on addn. of AcOH yields a reddish substance insol. in alkali and m. 205°; **N** dissolves in concd. alc. KOH with red color; after some hrs. the color fades out and there sep. faintly yellow needles contg. Cl, m. 119° after recrystn. from AcOH, dissolve in concd. HCl, are reprecip. by H₂O and dissolve in alc. KOH without color. **K**, needles from AcOH, m. 215° (decompn.). **L**, yellow plates from ligroin, m. 146°. **P**, red prisms from petr. ether, m. 158°. *α*-Phenylhydrazone of **J**, dark red needles from AcOH, m. 217–8° (foaming). Tetrachloromethylisatinoid (**Q**), m. 127°, solidifies about 180° and m. again around 222°, gives only a faint brown indophenin reaction, dissolves in hot NaOH, only very slowly in the cold, with a transient reddish brown color and yields **J** on acidification; it apparently belongs to the γ -series. In repeating the work on the Ag salt of **A**, it was found that in the rearrangement of the unpurified lactim into the Na isatol acidification of the filtrate gave *N*-benzoyl-5,7-dimethylisatinic acid, tetrahedrons from AcOH, m. 208° (decompn.), converted by hot Ac₂O into benzoyldimethylisatin, yellow platelets from AcOH, m. 172°. **R**, dark red prisms from ligroin, m. 140–1°. *α*-Phenylhydrazone of **A**, red rodlets from AcOH, m. 234° (decompn.). 5,7-Dimethylmethylisatoid (**S**), red plates from MeOH, m. 237° (decompn.), gives no indophenin reaction, dissolves in concd. HCl with orange-red color. *N*-Acetyl-7-methylisatin, from **U** boiled 20–30 min. in Ac₂O with 2–3 drops concd. H₂SO₄, yellow platelets from ligroin, m. 163°, regenerates **U** with boiling HCl, converted by alkalis into *N*-acetyl-7-methylisatinic acid, needles from AcOH, m. 175°. C. A. R.

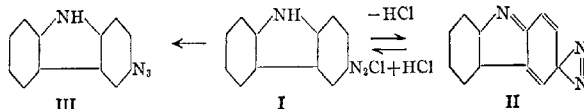
Complex metal compounds of indigo blue. K. KUNZ. Ber. 55B, 3688–91 (1922).—It was noticed previously (C. A. 16, 4208) that the blue-violet solns. of indigo in boiling *o*-O₂NC₆H₄Cl in the presence of CuCl and NaOAc became colorless with pptn. of very slightly sol. crystals. When this ppt. is heated above 200° in the absence of Cu, indigo blue is regenerated. The ppt. gives a normal indigo dye with alk. Na₂S₂O₄. It is decompd. by acids. After purification by NH₃, in which it is unchanged, the product may be recrystd. from boiling PhNH₂. Analysis gave 10.37% Cu. K. believes the substance to have the structure shown. A similar Zn salt, C₂₂H₁₈O₄N₂Zn, may be prepd. by



heating indigo with Zn in *o*-O₂NC₆H₄Cl at 240–50° (yield nearly quant.). With H₂O it hydrolyzes to indigo blue. There is no dye formation with air-free NaOH. Also a cryst. Ni compd., hydrolyzed by H₂O may be prepd. An attempt to prep. the Mg compd. was unsuccessful. J. D. BROWN

The diazo reaction in the carbazole series. Carbazole-3-diazoimine and -3-

diazonium salts. C. T. MORGAN AND H. N. READ. *J. Chem. Soc.* **121**, 2709-17(1922).—The outstanding features in regard to carbazole-3-diazonium salts are their stability compared with the corresponding diazo derivs. of C_6H_6 , Ph_2 and $C_{10}H_8$ series and their pronounced yellow color. *Carbazole-3-diazonium chloride* (I) was prepd. by adding 20% aq. $NaNO_2$ to a thin paste of the 3- NH_2 .HCl derivs. in dil. HCl at 8°; crystd. from H_2O it forms fan-shaped clusters of yellow needles with 2 mols. H_2O , which became green at 98° and decompd. 102°. The anhydrous salt darkened at 106-10° and decompd. explosively at 153°. The *chloroaurate*, bright yellow, sparingly sol. compd., is quite stable in the dark but darkened on exposure to light. Treated with NH_4OH in H_2O I gives *carbazole-3-diazoimine* (II), bright orange-red needles which, heated rapidly, exploded at 95°, but heated slowly, darkened between 80-105° and did not m. 300°. It decomp. almost at once in the sunlight and explodes on rubbing or by percussion or when placed near a flame. It is decompd. by H_2O , forming an ill defined product which does not m. 300°. HCl regenerated I. I or II, treated with β - $C_{10}H_7OH$, gave *carbazole-3-azo- β -naphthol*, reddish violet needles, m. 279° (decompn.); with resorcinol, *carbazole-3-azo-resorcinol*, violet, m. 265-70°. *Carbazole-3-azo- β -naphthylamine*, reddish brown needles, m. 280-3°. *Carbazole-3-diazocyanide*, $NH:C_{12}H_7N_2CN$, by the action of KCN upon I in acid or alk. soln., small, brick-red needles, decomp. 155-60°. The slow rate of condensation with β - $C_{10}H_7OH$ suggested the *anti*-form. *Carbazole-3-diazonium nitroprus-*



side, amorphous light yellow ppt. which becomes green at 150° and decomp. explosively at 160°. 3-*Triazocarbazole* (carbazole-3-azoimide) (III), by the action of NaN_3 , lustrous plates, m. 176-7° (decompn.). It becomes brown on exposure to light and decomp. with considerable violence when dropped into H_2SO_4 . *Ethyl carbazole-3-azoacetate*, golden yellow prismatic needles, m. 193°. *N-Ethylcarbazole-3-diazonium chloride*, golden yellow needles with 2 H_2O , m. 149-50° (decompn.). It is not very sensitive to the action of light. The *chloroaurate* is a bright yellow compd. The *dichromate* forms bright yellow acicular prisms and is comparatively stable. The *cyanide* forms bright red needles and decomp. 148-55°. The *nitroprusside* seps. as bright yellow microneedles. *Ethyl N-ethylcarbazole-3-azoacetate*, golden yellow needles, m. 125°. The action of NH_4OH on the chloride gave a light brown microcryst. product, charring at 150-5°, which is probably an external diazo oxide. Conc'd. HCl gave a greenish blue indefinite product and the chloride. C. J. West

3-Hydroxy-2-phenylindazole. GUSTAV HELLER. *Ber.* **55B**, 2680(1922).—H. does not agree with v. Auwers and Hüttenes (*C. A.* **16**, 3654) that Freundler's 3-hydroxy-2-phenylindazole, m. 214°, which dissolves in alkali with a bright yellow color, and H.'s isomer, m. 204°, sol. in alkali almost without color (*C. A.* **11**, 2778), are the same substance in different degrees of purity. C. A. R.

Some arylazoglyoxalines. F. L. PYMAN AND L. B. TIMMIS. *J. Soc. Dyers Colourists* **38**, 269-72(1922); cf. *C. A.* **13**, 1301; **14**, 275, 2334; **15**, 512, 513, 1501, 2440.—Expts. show that arylazoglyoxalines are true C-azo compds. and not diazoimino compds. The main products of coupling glyoxaline with diazonium salts in alk. soln. are 2-arylazoglyoxalines. 2-*o*-Methoxybenzeneazoglyoxaline forms orange prisms from alc., m. 161° to a red liquid, is insol. in H_2O , but sol. in alc., Et_2O , acetone, dil. mineral acids and aq. NaOH. It was prepd. by diazotizing 4.3 g. *o*-anisidine in 50 cc. H_2O and 10.5 cc. conc'd. HCl with 2.3 g. $NaNO_2$. This soln. was added to an iced soln. of 2.37 g. glyoxaline and 7.4 g. Na_2CO_3 in 170 cc. H_2O . The 4.2 g. ppt. was extd. with 0.2 N HCl and

repptd. fractionally by aq. NaOH, when the last 0.9 g. formed light yellow needles and upon recrystn. from alc. gave 0.71 g. pure compd. *2,4-Diamino-4-m-methoxyphenylglyoxaline dihydrochloride* crysts. from 10% HCl as anhyd. felted white silky needles which m. about 268° (decompn.), forms the picrate or sulfate upon treatment with the corresponding acid, is sol. in H₂O and was prepd. by reduction of 2.3 g. 2-*o*-methoxybenzencazoglyoxaline in 20 cc. boiling 2.5% HCl with 4.9 g. hydrated SnCl₂ in 12 cc. HCl. After decolorization, 20 cc. HCl were added and on cooling 2,4-diamino-4-*m*-methoxyphenylglyoxaline chlorostannate deposited. This was dissolved in H₂O, decompd. by H₂S, and the remaining soln. deposited 2.4 g. of the di-HCl salt upon concn. *2-p-Ethoxybenzeneazoglyoxaline* crysts. from alc. in brownish red plates, m. 216° to a red liquid, insol. in H₂O, sparingly sol. in alc., sol. in dil. mineral acids and aq. NaOH. It was prepd. by diazotizing 15.2 g. *p*-phenetidine in 95 cc. H₂O and 32 cc. concd. HCl with 9 g. NaNO₂ in 100 cc. H₂O. After 20 min. the soln. was stirred into 8.5 g. glyoxaline and 20 g. Na₂CO₃ in 625 cc. H₂O at 5°. After 24 hrs. on ice 23 g. ppt. was filtered off and extd. with dil. HCl; upon repptn. by Na₂CO₃ and recrystn. from alc. 17.2 g. *2-p*-ethoxybenzeneazoglyoxaline was obtained.

CHAS. B. MULLIN

Miscellaneous notes on the aldehyde compounds of hydroxyamines and on the partial*acylation of these amines. MAX BERGMANN, REINHOLD ULPTS and FRANCISCO CAMACHO. *Ber.* 55B, 2796-812(1922); cf. *C. A.* 15, 4007.—Compds. contg. both an NH₂ and a HO group are widely distributed in nature but methods for working with such compds. are still in great need of development. The aldehyde compds. of HO bases have been found useful for various purposes, especially for purifying and for partially acylating hydroxyamines. The structure of these compds. may vary considerably, depending on the nature of the HO base; considering only those formed by condensation of 1 mol. each of the components with elimination of H₂O, they may be either simple Schiff bases, oxazolidines (Knorr and Matthes, *Ber.* 34, 3483(1901)) or pentoxazolidines (Kohn, *C. A.* 10, 1039). Their usefulness for purposes of prepn. depends on the ease with which they are formed and again decomp. and on the great power of many of them to cryst. Thus, *p*-EtOC₆H₄NH₂ with ClCH₂CH₂OH and ClCH₂CH(OH)CH₂OH always gives, besides EtOC₆H₄NHCH₂CH₂OH (A) and EtOC₆H₄NHCH₂CH(OH)CH₂OH (B), resp., considerable amts. of the tertiary bases, *e. g.*, EtOC₆H₄N[CH₂CH(OH)CH₂OH]₂ (C), which, especially in the case of B and C, are difficult to sep., as neither can be distd. and both have about the same solubilities. With HCHO, however, only B reacts appreciably, forming, even at room temp., a cyclic compd. (D), probably EtOC₆H₄NCH₂CH(CH₂OH).OCH₂, which can be sepd. by distn. and, after elimination

of the HCHO, gives pure B without further purification. Instead of HCHO, which yields chiefly low-boiling products, may be used other aldehydes or even ketones. The results of the partial acylation of NH₂ alcs. and phenols through their aldehyde compds. also depend, of course, on the structure of the latter. The introduction of the acid residue can easily be limited to the HO group when the aldehyde compd. is of the Schiff base type, whereas if it is of the cyclic type the acylation product, after elimination of the aldehyde, will be a hydroxylated acid amide. Another entirely different way of acylating HO bases on the N consists in treating them with acid polysulfides, (RCO)₂S_n (*n* = 1 to 4; cf. *C. A.* 14, 3414): Bz₂S₂ + 2RNH₂ = 2BzNHR + H₂S + S; these sulfides practically do not at all attack alc. or phenol HO groups. Often it will be found necessary, whether it is desired to acylate the HO or the basic group, to acylate both and to remove subsequently the one or the other of the acyl groups. A means of selectively removing the *N*-acyl group is furnished by the action of PCl₅ and alc. (*C. A.* 15, 3277) whereby acid amides can be converted, through the imide chlorides and, probably, the imido esters as intermediate products, into a salt of the base in one operation. In this way, *o*-BzOC₆H₄NH₂.HCl (E) can be obtained in good yield from BzOC₆H₄-

NHBz. **E** in acid soln. is not so unstable as might be concluded from previous fruitless attempts to prep. it, but it at once changes into $\text{HO}_2\text{CC}_6\text{H}_4\text{NHBz}$ when the base is liberated from its salts or when the **E** is heated to its m. p., heated with H_2O or treated with NaOAc in the cold; in the latter case it is simultaneously partly converted into 2-phenylbenzoxazole. The oxazolidines and pentoxazolidines in whose formation HCHO has taken part occupy a peculiar position in that the HO bases from which they are derived easily undergo further change when treated in acid soln. with HCHO . Thus, while **A** and **B** in the cold and in neutral soln. form oxazolidines (**D**), on gentle warming in the presence of acid, the HCHO bridge in the **D** is broken and the **N** is methylated, giving $\text{EtOC}_6\text{H}_4\text{NMeCH}_2\text{CH}_2\text{OH}$ (**F**) and $\text{EtOC}_6\text{H}_4\text{NMeCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ (**G**), resp. Not the least indication of an oxidation of the alc. groups to aldehyde or ketone groups, as in the case of Hess's hydramines (*C. A.* 10, 467), was noted. Using essentially Reddelien and Danilof's method (*C. A.* 16, 1761), excepting that a much more dil. alkali (0.5 *N*) was employed and that the BzCl was dild. with Et_2O , *p*- $\text{H}_2\text{NC}_6\text{H}_4\text{OBz}$, m. 148°, was obtained in 70% yield from $\text{H}_2\text{NC}_6\text{H}_4\text{OH}$ through the deriv. $\text{PhCH:NC}_6\text{H}_4\text{OH}$, 2,4,5-Triphenyloxazolidine (Erlenmeyer's "benzylideneisodiphenyloxyethylamine" (*Ann.* 210, 379(1881)) with BzCl in $\text{C}_6\text{H}_6\text{N}$ and subsequent treatment of the product with alc. HCl on the H_2O bath gave isodiphenyloxyethylamine *N*-benzoate, m. 225°. *N*-Benzoyl-*t*-tyrosine, 6-sided tables from $\text{EtOH-H}_2\text{O}$, m. 164°, was prepd. from its Et ester, 6-sided elongated tables from C_6H_6 , m. 120-1°, which in turn was obtained almost quant. from *t*-tyrosine Et ester and Bz_2S_2 refluxed 0.5 hr. in alc. *o*- $\text{HOC}_6\text{H}_4\text{NHBz}$, tables from MeOH , m. 169-71°, was similarly obtained from $\text{HOC}_6\text{H}_4\text{NH}_2$ and Bz_2S_2 , as was also the *p*-compd. *o*- $\text{BzNHC}_6\text{H}_4\text{OBz}$, m. 179°, obtained in 90% yield from $\text{H}_2\text{N-C}_6\text{H}_4\text{OH}$ and 2 mols. BzCl in $\text{C}_6\text{H}_6\text{N}$, gives with PCl_5 at 100° 89% of **E**, fine felted needles from $\text{AcOH-HCl-Et}_2\text{O}$, m. 149°, couples, after diazotization, with PhNMe_2 , giving a dye $\text{BzOC}_6\text{H}_4\text{N:NC}_6\text{H}_4\text{NMe}_2$, red plates from alc., m. 116°. Reduction of $\text{O}_2\text{NC}_6\text{H}_4\text{O-Bz}$ with Sn and cold alc. HCl does not give **E** but 2-phenylbenzoxazole, and the same result is obtained from **E** under identical conditions. 3-*p*-Ethoxyphenyl-5-methyloloxazolidine (**D**), b. 0.2-0.4 135-45°, m. 57-9°, gives in alc. with $(\text{CO}_2\text{H})_2$ the oxalate, m. 161-3°, of *N*-β,γ-dihydroxypropyl-*p*-phenetidine (**B**), m. 90-2°, which with HCHO and HCl on the H_2O bath yields a compound m. 51-3° which is apparently the Me deriv. **G** with 0.5 H_2O ; it does not react with the usual C:O reagents, does not redden fuchsin- SO_2 and contains no HCHO easily split off; it is also obtained from $\text{EtOC}_6\text{H}_4\text{NHMe}$ and glycidic. The oxazolidine $\text{EtOC}_6\text{H}_4\text{N-CH}_2\text{CH}_2\text{O-CH}_2$, from $\text{EtOC}_6\text{H}_4\text{NH}_2$ and $\text{ClCH}_2\text{CH}_2\text{OH}$ and subsequent

treatment with HCHO , b. 140°, m. 78-80°, gives the acid oxalate, flat spears, m. 139-40°, of *N*-β-hydroxyethyl-*p*-phenetidine (**A**), b. 150-5°, leaves, m. 50-1°, easily sol. in dil. acids, which gives with BzH at 50° 2-phenyl-3-*p*-ethoxyphenyloxazolidine, fine needles from alc., m. 72-3°, and with HCHO and HCl *N*-methyl-*N*-β-hydroxyethylphenetidine (**F**), b. 130°, m. 38-9° (yield, about 60%), converted by BzCl in $\text{C}_6\text{H}_6\text{N}$ into the benzoate, microprisms or 6-sided tables, m. 78°.

C. A. R.

Pyridine derivatives of diacetonitrile and benzoacetonitrile. ERICH BENARY AND GERTRUDE LÖWENTHAL. *Ber.* 55B, 3429-34(1922).—Attempts to discover whether the reaction whereby Et 4'-cyanodihydrocollidinedicarboxylate (cf. *C. A.* 15, 1314), in the course of its prepn. from the chloride, or by the action of alc. KOH , was converted into a pyrrole deriv., was of more general significance have thus far been unsuccessful. 4'-Chlorodihydrocollidinedicarboxylic nitrile (**A**) was prepd., in 45% yield by the reaction of 5 g. diacetonitrile on 5 g. $(\text{ClC}_2\text{H}_4)_2\text{O}$, with cooling, followed by pptn. with 10% NH_4OH , plates from MeOH , m. 170°. Boiled with KCN in MeOH , it forms a mixt., separable after concn., by fractional recrystn. from EtOH , into 4'-cyanodihydrocollidinedicarboxylic nitrile (**B**), the less sol. (hard crystals m. 220°, insol. in H_2O , slightly in HOAc , and unchanged by boiling with alc. KOH), and 4'-carbaminodihydrocollidine-

dicarboxylic nitrile (C), colorless plates, m. 109° , sol. in HOAc, insol. in H_2O ; on boiling C with KOH, NH_3 is evolved, and the residue m. 280° . B, oxidized in HOAc with $NaNO_2$ (cooling), gives *4'-cyanocolidinedicarboxylic nitrile*, plates from H_2O , m. 230° (decompn.), sol. in EtOH, Me_2CO , dil. H_2SO_4 , less sol. in hot H_2O . A in concd. HOAc soln., on addn. of $NaNO_2$, and pptn. with H_2O , forms the *oxime of 4'-aldehydocolidinedicarboxylic nitrile* (D), unstable in boiling Me_2CO and EtOH, prismatic needles from MeOH, browning at 157° , m. 161° (decompn.), has acid properties, is unstable in soln. Shaken with BzCl in alk. soln. it gave the *benzoyl derivative*, needles or plates from EtOH, sintering 176° , m. 186° . With Ac_2O an *acetyl derivative* is formed, crystals from H_2O , m. 115° . *4'-Chloro-2,6-diphenyldihydro- γ -picoline-3,5-dicarboxylic nitrile* (E), prepd. from diacetonitrile and benzoacetonitrile, plates from MeOH, m. 235° . By oxidizing E with 2 parts concd. HNO_3 , and pptg. with H_2O is obtained *4'-chloro-2,6-diphenyl- γ -picoline-3,5-dicarboxylic nitrile* (F), crystals from EtOH, m. 177° , insol. in dil. HCl, Et_2O and gasoline. *4'-Cyano-2,6-diphenyldihydro- γ -picoline-3,5-dicarboxylic nitrile*, prepd. from E by boiling with KCN, plates from EtOH, m. 185° . *4'-Hydroxymethyl-2,6-diphenylpyridine-3,5-dicarboxylic nitrile* is formed by boiling F with 20% KOH, needles from EtOH, m. 176° , insol. in H_2O , Et_2O and gasoline. On standing with alc. NH_3 , E yields *4'-amino-2,6-diphenylpicoline-3,5-dicarboxylic nitrile imidolactam*.

I. P. ROLF

Mechanism of syntheses of isoquinoline derivatives from derivatives of benzylamine. PAUL STAUB. *Helvetica Chim. Acta* 5, 888-94 (1922).—S. preps. $NO_2CH_2CH(OH)Me$ (A) from $MeNO_2$ and AcH according to Henry (*Compt. rend.* 120, 1205 (1895)) in 38% yield, and gives a modification yielding 52%. Reduced with Al-Hg in neutral soln., A gave 76% of the NH_2 alc. (B), which was condensed with BzH (4 hrs. on the H_2O bath) to α -benzalaminoisopropyl alcohol (C), b_p $132-41^{\circ}$, m. 76° . B, heated 4 hrs. at $110-30^{\circ}$ with $PhCH_2OH$, gave $PhCH_2NHCH_2CHMeOH$ (D), b_p 142° . $PhCH_2NHSO_2Ph$ (E) heated 7 hrs. at 170° with $(CH_3)_2O$ gave $PhCH_2N(SO_2Ph)CH_2CH_2OH$ (F) (not purified). Benzyl- β -bromoethylphenylsulfonamide (G), m. 83° , was formed (40%) from $C_6H_4Br_2$ and the Na salt of E. Similarly, benzylphenacylphenylsulfonamide (H) (amorphous, not analyzed) was made from $PhCOCH_2Br$ (J). J and $PhCH_2NNaAc$ gave benzylphenacylacetamide (K) (thick sirup; not analyzed). All attempts to make isoquinoline (L) by standard methods of ring-closure from C, D, F, G, H, or K, failed completely. S. concludes that to form L (or its derivs.) from a nucleus $Ph-C-N-C-C-$, one must have: (a) a system of conjugated double bonds, or the possibility of forming such a system; (b) an OH or OR group in the β -position to the N. Fischer's synthesis of L (*Ber.* 26, 764 (1893)) is interpreted in this sense.

BRN H. NICOLET

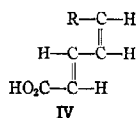
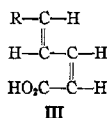
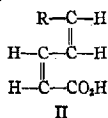
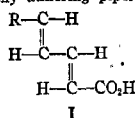
Reactivity of methyl groups in heterocyclic bases. WM. H. MILLS and J. L. B. SMITH. *J. Chem. Soc.* 121, 2724-37 (1922).—Investigation of isoquinoline and thiazole derivs. has shown that the properties of a Me group adjacent to the cyclic N atom in bases of this type differ in the most marked manner according to the side of the N atom on which the group is situated. *1-Styrylisoquinoline*, needles, m. 111° , is readily formed by condensation of $1-MeC_6H_4N$ with BzH with $ZnCl_2$ (100° for 20 hrs.) while $3-MeC_6H_4N$ could not be made to condense with BzH. *1-Methylisoquinoline methiodide* (A), needles, m. 207.5° , condenses with $p-Me_2NC_6H_4CHO$ to give *1-p-dimethylaminostyrylisoquinoline methiodide*, light red needles with faint blue reflex, m. 257° (decompn.). The orange color of the dil. soln. is discharged by acids but reappears on diln. or addn. of alkali. The dye is a weak photosensitizer. A, heated with $Me_3NC_6H_4NO$ and C_6H_5N in EtOH, gives a deep ruby color; $EtONa$ and $C_6H_7N.MeI$ give an intense red color and the soln. shows the double absorption band in the green characteristic of the isocyanines. These color reactions provide an exceedingly delicate test for the reactivity of a Me group in bases of the type under consideration. *3-Methylisoquinoline methiodide*, lustrous golden

needles, m. 219°, showed none of the condensation reactions of the 1-isomer. *4-Phenyl-2-thiazolylphthalonimethane*, from 4-phenyl-2-methylthiazole, $C_6H_4(CO)_2O$ and $ZnCl_2$, light brown shining needles, m. 257°. Dil. alc. solns. dye silk a faint yellow shade. *4-Phenyl-2-methylthiazole methiodide* (B), shining needles, m. 202°, condenses with *p*- $Me_2NC_6H_4CHO$ in abs. alc. to form *4-phenyl-2-p-dimethylaminostyrylthiazole methiodide*, ruby-red crystals with bluish green metallic reflex, decomp. 243°; the color in dil. solns. is deep orange, and is discharged by acids. The dye is a photosensitizer and the extra sensitiveness extends to $\lambda 6200$ with a max. at $\lambda 5500$ for moderate exposure. $Me_2NC_6H_4NO$ gives *4-phenylthiazole-2-aldehyde p-dimethylaminoanil methiodide*, red, with an intense green metallic reflex, decomp. 228°. The deep ruby-red color of solns. is discharged by acids. *4-Phenyl-3-methyl-2-thiazoleryl-4-quinolylmethane methiodide*, by condensing with C_6H_7NMeI , forms red crystals with a bluish green metallic reflex, decomp. 240°. The extra sensitiveness extends to $\lambda 6000$ with a max. at $\lambda 5300$. 2-Phenyl-4-methylthiazole (*Ann.* 259, 236) $b_{702} 282^\circ$, m. 29.5°. It did not condense with BzH . The *methiodide*, faintly yellow prisms, m. 192°, formed with far less readiness than the isomeric compd. It did not show the condensation reactions described above for B. It is also possible to consider this difference in reactivity from the aspect of tautomeric change. It may be regarded as indicating that passage into a reactive form is possible when the Me group is in the 1-position but not when it is in the other.

C. J. WHEAT

Natural and artificial pepper substances. II. The chavicin of pepper resin, the especially active constituent of black pepper. ERWIN OTT AND FRITZ EICHLER (WITH OTTO LÜDEMANN AND HEINRICH HEIMANN). *Ber.* 55B, 2653-63(1922); cf. C. A. 16, 1229.—By hydrolysis with alc. KOH Buchheim obtained from chavicin (A) the especially active constituent of black pepper, piperidine (B) and a resinous acid, chavincinic acid (C) (*Arch. exp. Path. Pharm.* 5, 455(1876)), but as he showed the formation of B only qual. his work did not establish that A is the piperidine of C and his investigations have accordingly been taken up again. The pepper resin was prepd. and purified essentially by his method but it was found to be absolutely necessary, before sepg. the last of the piperine (D), to remove the ethereal oils (0.5% of the pepper) with the greatest care by repeated distn. with steam. Only in this way it is possible to sep. the D practically completely (3.6%) by taking up the resin in Et_2O in which it is sol. in all proportions. The compn. of the resin so obtained (0.8%) already showed a striking similarity to that of D (C and H 1.75 and 3% too high, N 0.2-0.5% too low); sapon. showed that the difference was due to the presence of not inconsiderable amts. of waxes and presumably also of chlorophyll; alc. KOH gave 71% B, calcd. on the assumption that the resin is isomeric with D. In view of the facts that the resin still contained the above mentioned impurities and that other piperidides of unsatd. acids, such as pure D and cinnamic piperidide, hydrolyzed under the same conditions, never gave more than 90-2% of the B contained in them, it follows that A is indeed a piperidide. C, the other component of A, was obtained as a semisolid mass, permeated with resinous constituents, by pptn. from the strongly alk. soln., previously freed of B and wax alcs. by steam distn. and of unsapon. resin by extn. with Et_2O . Freed from the dark brown, easily sol. impurities with a little cold C_6H_6 and repeatedly recrystd. from boiling C_6H_6 it yields a yellow finely pulverulent and at the same time granular acid, designated *isochavincinic acid* (E) since, from its slight soly., it is evidently no longer identical with the exceedingly sol. C but has been formed from it by rearrangement. E in its properties greatly resembles piperinic acid (F); it is somewhat more sol. in alc. and C_6H_6 , is of a somewhat darker yellow color and m. somewhat lower (200-2°). Under the microscope it can be distinguished from F with certainty, being completely amorphous (spherical aggregates), but the compn., mol. wt. and titration value and the amt. of H taken up in the presence

of Pd (4 atoms, with formation of tetrahydropiperinic acid) are the same for E and F; the 2 acids must therefore be geometrical stereoisomers. Of the 4 theoretically possible isomers (I-IV) (R = piperonyl), the *trans-trans* form I corresponds to F, m. 217°, and the *cis-trans* form III to isopiperinic acid, m. 145°, synthesized by the elimination of CO₂ from piperonylidene malonic acid (G). Owing to its similarity to F, E must also contain at least one *trans* arrangement and therefore have the structure IV; for C there remains the *cis-cis* structure II. The conclusion that A and D are 2 opposite geometrically isomeric ethylene derivs., A being the *cis*-form, is confirmed by their great difference in soly. and m. p. and by the much more pronounced physiol. action of A. G m. 223° (Scholtz, *Ber.* 28, 1190 (1895), gives 204-5°, but in the prepn. of his sample he used a piperonylacrolein m. 70°, while O. and E. used a prepn. m. 80-3°, carefully recrystd. and freed from any adhering piperonal).



C. A. R.

Pilocarpine. V. Isomerism of pilocarpine and isopilocarpine. MAX POLONOVSKI AND MICHEL POLONOVSKI. *Bull. soc. chim.* 31, 1314-30 (1922); cf. C. A. 17, 763.—Possible explanations of the isomerism of pilocarpine (A) and isopilocarpine (B) are discussed in much detail. A study of the catalytic change of A to B by NaOEt (C) in abs. alc. shows that the reaction goes completely in the cold with a slight excess of C. When much C is used, the change in $[\alpha]_D$ is complete only after 48 hrs., as the isomerization is followed by a slower hydrolysis of the lactone grouping. Similar results were obtained with nitropilocarpine. When the lactone group in A is previously hydrolyzed, and the Na pilocarpate treated with C in abs. alc., no isomerization takes place; the same is true for Na nitropilocarpate, and for Et γ -chloropilocarpate. It is concluded that alkali rearranges A to B (etc.) only when the lactone group remains intact; and that the change is probably only a racemization of one of the asym. C atoms (a) or (b) in

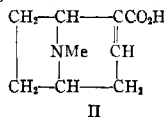
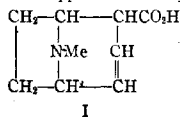
(a) (b)

$\text{CH}_2.\text{O.CO.CHEt.CHCH}_2\text{C}:\text{CH.NMe.CH:N}$). It is suggested that (b) is the C atom

concerned; but the reason for this choice is not clear.

BEN. H. NICOLET

Egonine. J. GADAMER AND C. JOHN. *Arch. Pharm.* 259, 227-44 (1921-2).—Of the 2 formulas applicable to anhydroegonine, Willstaetter decided in favor of I,



but it now appears that II must be the correct one, since hydroegonidine is formed on reduction in at least 2 different optical isomerides. This could only result through creation of a 3rd asym. C atom, a condition impossible in the case of formula I, unless the occurrence of isomerization is assumed during reduction. If carried out by the Willstaetter method (Na and AmOH) such isomerization is conceivable, but 2 hydroegonidines were likewise obtained through hydrogenation *via* Paal and Skita, where isomerization is improbable. In every case the chloroaurates were employed to sep. the optical isomerides. The Et esters of the various chloroaurates likewise served as further confirmation. Hydroegonidine, obtained by reducing the HBr addn. product

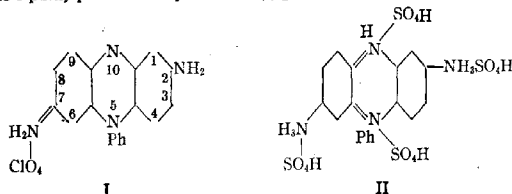
of anhydroecgonine, proved to be an entity identical with one of the isomerides prep'd. via Paal and Skita. Formula II, contg. as it does a conjugated system of double bonds, justifies the expectation of an increase in the mol. refraction, as compared with its reduction product hydroecgonidine. Detn. of the mol. refractions in the case of the esters showed the exaltation expected, although the Et ester of anhydroecgonine considered by itself gave an actual depression, a phenomenon attributable doubtless to the pyrrolidine ring. The following substances were prep'd. and characterized during the investigation. Hydroecgonidine-HCl, via Willstaetter, m. 233-4°, $[\alpha]_D -3.0^\circ$, yielding 2 chloroaurates m. 210° and 230°, resp., which on reconversion into hydroecgonidine-HCl gave 2 corresponding isomerides, both m. 233-4°, but showing $[\alpha]_D -2.7^\circ$ and -4.4° , resp. Reduction via Paal and Skita yielded a product convertible into 2 chloroaurates m. 210° and 220°, resp., which latter on reconversion gave 2 hydroecgonidine hydrochlorides showing $[\alpha]_D -2.30^\circ$ and 1.24° , resp. The hydroecgonine-HCl prep'd. by reducing the HBr addn. product of anhydroecgonine with Zn and H_2SO_4 yielded only 1 chloroaurate m. 210°, $[\alpha]_D 2.78^\circ$. The chloroaurate m. 210° gave an Et ester m. 173-4°, and the chloroaurate m. 220°, an Et ester m. 123°. The Et ester prep'd. from the *d*-rotatory chloroaurate m. 173-4° yielded an ester-HCl showing $[\alpha]_D 5.1^\circ$. Anhydroecgonine Et ester is an oil $b_D 137-9^\circ$ (cryst. hydrochloride m. 243-4°). H_2SO_4 or HSO_4Cl converts *l*-ecgonine into the sulfuric ester, crystals, m. 258-60°, $[\alpha]_D -85^\circ$ (chloroaurate, $C_8H_{10}O_6NS.HAuCl_4.2H_2O$, m. 110° (anhydrous 152-3°)). Similar treatment of anhydroecgonine failed to yield the corresponding deriv. W. O. E.

The additive formation of four-membered rings. I. The synthesis and division of derivatives from 1,3-dimethindiazidine. C. K. INGOLD AND H. A. PIGGOTT. *J. Chem. Soc.* 121, 2793-804 (1922).—The word "division" is used to indicate the cutting of a ring asunder (at 2 points) as compared with fission and scission, the cutting of a ring at one point. The present work is an examn. of the conditions of formation and the stability of the 1,3-dimethindiazidine ring. 3-*p*-Bromophenyl-2-*p*-hydroxyphenyl-1,4-diphenyl-1,3-dimethindiazidine, from $p\text{-HOC}_6\text{H}_4\text{CH:NPh}$ and $\text{PhCH:NC}_6\text{H}_4\text{Br}$, pale green glistening leaflets, m. 165-7°; when fused for a short time or heated in EtOH it yields *p*-hydroxybenzylidene-*p*-bromoaniline, small, pale yellow needles, sepd. by its insoly. in C_6H_6 and PhCH:NPh . 3-*m*-Nitrophenyl-2-*p*-hydroxyphenyl derivative, long felted orange needles, m. 178°; on division as above this yields *p*-hydroxybenzylidene-*m*-nitroaniline, short, stout needles, m. 190-1°, and PhCH:NPh . 3-*o*-Nitrophenyl-2-*p*-nitrophenyl derivative, fine, buff-colored needles, m. 163-5°; this yields on division *p*-nitrobenzylidene-*o*-nitroaniline, bright yellow microneedles, m. 118°, and PhCH:NPh . *m*-Nitrobenzylidene-*p*-bromoaniline, very pale yellow prisms, m. 84-5°. In the reactions (a) $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NPh} + p\text{-BiC}_6\text{H}_4\text{:CHNPh}$ and (b) $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NC}_6\text{H}_4\text{Br} + \text{PhCH:NPh}$, identical results were obtained. *p*-Nitrobenzylidene-*p*-nitrobenzylamine (A), needles, m. 150°. *m*-Nitrobenzylidene-*m*-nitrobenzylamine (B), glistening leaflets, m. 141°. A mixt. of $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p$ (C) and $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}m$ (D) in EtOH gave A and B; similarly a mixt. of A and B gave C and D. *m*-Nitrobenzylidene-*o*-nitroaniline (E), bright yellow feathery crystals, m. 143-5°. In the reaction of $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NPh} + o\text{-O}_2\text{NC}_6\text{H}_4\text{:CHPh}$, the change to E and PhCH:NPh takes place in C_6H_6 after several weeks at room temp. *m*-Nitrobenzylidene-*m*-nitroaniline, pale buff-colored needles, m. 158°, is formed, together with PhCH:NPh by the reaction of $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NPh}$ and $m\text{-O}_2\text{NC}_6\text{H}_4\text{:N:CHPh}$ for 48 hrs. *m*-Nitrobenzylidene-*p*-nitroaniline, aggregates of olive-yellow needles, m. 145-6°, is formed after the reaction of $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NPh}$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{:N:CHPh}$ for 1 month. Indications of the formation of a cycloid were obtained but it could not be isolated in a pure condition. Similarly $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NPh}$ and $m\text{-O}_2\text{NC}_6\text{H}_4\text{:N:CHPh}$ gave PhCH:NPh and $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NC}_6\text{H}_4\text{NO}_2\text{-}m$; $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NPh}$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{:N:CHPh}$

gave PhCH:NPh and $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{C}_6\text{H}_4\text{NO}_2$; $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NPh}$ and $p\text{-BrC}_6\text{H}_4\text{N:CHPh}$ gave PhCH:NPh and $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{C}_6\text{H}_4\text{Br}$; $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{Ph}$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{N:CHPh}$ gave $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{C}_6\text{H}_4\text{NO}_2$ and $\text{PhCH:NCH}_2\text{Ph}$; $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{Ph}$ and $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{N:CHPh}$ gave $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{C}_6\text{H}_4\text{NO}_2$ and $\text{PhCH:NCH}_2\text{Ph}$. The reaction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{Ph}$ and $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{N:CHPh}$ gave $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{C}_6\text{H}_4\text{NO}_2$ and $\text{PhCH:NCH}_2\text{Ph}$. Finally the reaction of $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{Ph}$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{N:CHPh}$ gave $m\text{-O}_2\text{NC}_6\text{H}_4\text{CH:NCH}_2\text{C}_6\text{H}_4\text{NO}_2$ and $\text{PhCH:NCH}_2\text{Ph}$. These expts. confirm the hypothesis: In double-bonded compds. there exists a general tendency towards the establishment, in the liquid state or in soln., of an equil. with the dimeric form: $2\text{A} : \text{B} \rightleftharpoons \text{A-B-A-B}$. In most of these cases the formation of the cyclic substances in the

equilibrated soln. was relatively small, so that the isolation of the intermediate diazidine was possible only in those instances in which the 2 successive changes proceeded at a small velocity. . . . C. J. WEST

Determination of the structural formulas of dyes by examination and discussion of their absorption spectra. IV. F. KEHRMANN AND M. SANDOZ. *Helvetica Chim. Acta* 5, 895-905(1922); cf. *C.A.* 14, 1300; 16, 103.—Absorption spectra are given and interpreted for various salts of a series of diaminophenylphenazonium bases. 2,7-Diamino-5-phenylphenazonium perchlorate (I) gives a blue soln. in alc.; this corresponds



to the introduction of the auxochromic NH_2 group into aposafranine (B), justifying the p -quinonoid structure previously given for B. On adding a little H_2SO_4 the soln. becomes red, resembling solns. of B; the auxochromic power of the group NH_2 is destroyed, indicating that this group is the *second* to form a salt, and that the structure is still p -quinonoid. In concd. H_2SO_4 I forms a green soln., resembling the di-salt of B; this indicates that the 10-N is the *third* basic group to take part in salt-formation, also that, since "fixation of acid on a doubly bound atom which is part of a chromogen group causes a deepening of color, insofar as the original system of valences is not destroyed," this tri-salt has still the p -quinonoid structure. In fuming H_2SO_4 I is reddish brown. This corresponds to a tetra-salt of a color similar to that of phenylphenazonium disulfate, and indicates an o -quinonoid structure (II). By similar reasoning, the corresponding salts of the isomeric 1,3- and 3,7-diaminophenylphenazonium bases (C and D, resp.) are quinonoids of the following types; mono-salts, both *para*; di-salts, both *para*; tri-salts, C *ortho*, D *para*; tetra-salts, both *ortho*. Furthermore, the di-salt of D is held to involve the 7- and 10-, not the 3- and 7-N atoms, as might be expected. Mono-salts corresponding to the mono-Ac derivs. of A and C are p -quinonoids, whereas di-Ac derivs. give salts (on the 5-N) which are o -quinonoids. Spectra are also given for 3,7-diamino-5-methylphenazonium salts, and for certain of their substitution products. Three misprinted structural formulas (referred to by number only) tend to confuse the article.

BEN. H. NICOLET

Dyes derived from α,α' -dicyanodibenzyl diketone. SEKHIBHUSHAN DUTT AND N. K. SEN. *J. Chem. Soc.* 121, 2663-7(1922).—The action of EtONa upon a mixt.

of PhCH_2CN and $(\text{CO}_2\text{Et})_2$ in EtOH or of Na upon the mixt. without alc., gives α, α' -dicyanodibenzyl diketone $(-\text{COCHPhCN})_2$, brilliant yellow, glistening leaflets, m. 132° (cf. Vollhard, *Ann.* **282**, 4, who describes it as olive-green needles, m. 272°). Its identity is supported by the fact that it condenses with o -diamines to form azines. The following α, α' -dicyano-2,3-dibenzyl derivatives were prepd. by condensing with diamines in glacial AcOH . From $(-\text{CH}_2\text{NH}_2\text{HCl})_2$, 5,6-dihydropyrazine, very pale yellow needles, m. 155° . Quinoxaline, from $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$, brilliant yellow, glistening needles, m. 227° ; the concd. H_2SO_4 soln. is blood-red and wool is dyed a bright yellow shade. 8-Methylquinoxaline, from 2,3- $(\text{H}_2\text{N})_2\text{C}_6\text{H}_3\text{Me}$, brilliant orange-red needles, decomp. above 250° ; the concd. H_2SO_4 soln. is violet and wool is dyed orange-red shades. 1,4-Naphthoquinoxaline, from 1,2- $\text{C}_{10}\text{H}_6(\text{NH}_2)_2$, bright orange-yellow needles, m. 230° , dyeing wool orange-yellow shades and giving a violet color in concd. H_2SO_4 . 7-Aminoquinoxaline, from 1,2,4- $\text{C}_9\text{H}_6(\text{NH}_2)_3$, yellowish brown needles, sol. in concd. H_2SO_4 with a violet color and dyeing wool violet shades. 1,4-Naphthoquinoxaline-7-sulfonic acid, glistening yellow needles, decomp. above 270° ; it dyes wool intense yellow shades. 10-Hydroxy-1,4-naphthoquinoxaline-8-sulfonic acid, yellowish brown amorphous powder, sol. in concd. H_2SO_4 with a reddish violet color, and dyeing wool chocolate shades from a 2% Na_2CO_3 bath. 1-Phenylquinoxalinium chloride, from $o\text{-HCl.H}_2\text{NC}_6\text{H}_4\text{NHPH}$ in glacial AcOH-HCl , fine yellow needles, sol. in concd. H_2SO_4 with an orange-yellow color and dyeing wool bright yellow shades. 1-Phenyl-1,4-naphthoquinoxalinium chloride, orange-yellow microneedles, dyeing wool orange shades. 1- α -Naphthylquinoxalinium chloride, red microneedles, sol. in concd. H_2SO_4 with a reddish violet color and dyeing wool bright red shades. 1-*p*-Tolyl-6-methylquinoxaline, shining brown needles, dyeing wool brown shades. 6-Anilino-1-phenylquinoxalinium chloride, bluish green microneedles, sol. in concd. H_2SO_4 with a green color and dyeing wool fine bottle-green shades.

C. J. Wessr

Residual affinity and coordination. X. Salicylatotetramminocobaltic salts and the constitution of oxonium compounds (MORGAN, SMITH) 6. Models to illustrate a few principles of symmetry in teaching stereochemistry (MOHR) 2. Preparation of active Ni catalysts (BROCHET) 2. Chemical and pharmacological aspects of unsaturated radicals (BRAUN, LEMKE) 11H. Vat dyes of the azo series (MUKERJI) 25. Composition of paraffin wax (FRANCIS, *et al.*) 22. Halogenated hydrocarbon mixtures (U. S. pat. 1,440,976) 22.

NIELSEN, KAJ.: *Organisk Kemi*. Copenhagen: Frimodt. 54 pp. Kr. 1.75.

RIPEL, JOH.: *Grundlinien der Chemie für Oberrealschulen*. Vol. II. Organische Chemie. 212 pp. M 40.

ZIELINSKI, W. J.: *Chemie organiczna*. Warsaw: Nakl. Trzaski, Everta i Michalskiego. '81 pp. Mkp. 180.

Methane. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING. Brit. 186,900, Aug. 31, 1922. Addition to 146,110 (C. A. **14**, 3428). The process described in the principal patent for the production of CH_4 from CO and H is modified by introducing CO_2 into the gas mixt. either before the reaction starts or before it is completed. The theoretical proportions of CO and H , namely 1 : 3, may then be employed. Examples are given. Cf. 146,114 (C. A. **14**, 3428), and 161,924 (C. A. **15**, 2444).

Methane. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING. Brit. 186,899, Aug. 30, 1922. A mixt. of water vapor with CO or a gas, such as water-gas, contg. CO is passed over two Ni contacts or sets of contacts in series, the H_2O vapor being

removed from the mixt. between the two contacts. After elimination of CO_2 , the product consists of pure CH_4 or CH_2 , admixed with a little H. For the second contact, Ni obtained from calcined Ni nitrate and maintained at a temp. of $350\text{--}400^\circ$ may be used; preferably, however, the Ni is prepd. from Ni carbonate or org. Ni compds. and is employed at a temp of about 300° .

β -Thionaphthisatin. SOC. ANON. POUR L'IND. CHIM. À BAËLE. Brit. 188,850, Dec. 1, 1921. β -Thionaphthisatin is prepd. by the reaction of oxalyl chloride on β -thionaphthol in the presence or absence of diluents or condensing agents. According to examples, β -thionaphthol is boiled with excess of oxalyl chloride, boiled with oxalyl chloride in CS_2 soln., with or without further treatment with AlCl_3 , or treated in the cold with oxalyl chloride in the presence of concd. H_2SO_4 .

Ether. F. E. LICHTENTHAELER. Brit. 187,347, July 27, 1921. App. for the manuf. of ether comprises a plurality of conduits through which alc. vapors are caused to pass, each conduit having a series of intermediate chambers for the reception of H_2SO_4 , which flows countercurrent-wise and to which the alc. vapors are exposed as they pass through the conduits. The conduits are contained in a pressure chamber through which steam is passed in order to maintain them at the reaction temp. The pressure chamber with steam inlet and outlet pipes contains a no. of conduits, each composed of a plurality of chambers having retaining decks for H_2SO_4 and vapor caps. The conduits are made tight to the top and bottom decks of the pressure chamber, and a dome is provided into which the vapors pass. A steam-jacketed receptacle for the spent acid also serves as a distributing chamber for the alc. vapor admitted through the inlet. A uniform level of spent acid is maintained by a drain pipe surmounted by vapor seal. H_2SO_4 from a supply pipe is fed to the top of each conduit through feed-pipes provided with acid seals. The provisional specification refers also to the use of oil or other heating medium in the heating jacket.

Removing moisture from organic nitrates. W. O. SNELLING and W. R. LAMS. U. S. 1,441,130, Jan. 2. Wet materials such as nitrostarch are mixed with dry NH_4NO_3 or a similarly acting H_2O -sol. hygroscopic solid material which takes up a portion of the moisture present and forms a soln. which is drawn off.

Purifying naphthalene. D. F. GOULD. U. S. 1,441,417, Jan. 9. Impure molten C_{10}H_8 is agitated with concd. H_2SO_4 , the acid is drawn off, the C_{10}H_8 is permitted to solidify on cooling and comminuted and washed with dil. NaOH soln. Fluorene or $\text{C}_{14}\text{H}_{10}$ may be similarly purified.

Purifying isopropyl ether. H. E. BUC. U. S. 1,442,520, Jan. 16. The ether is mixed with H_2SO_4 of 65–80% strength, the soln. is dild. by addn. of H_2O and the ether is sepd. from the dild. soln. by stratification and distn.

Normal propyl chloride. C. O. JOHNS and H. E. BUC. U. S. 1,440,683, Jan. 2. Normal propyl chloride is prepd. by introducing HCl into normal propyl alc., distg. the mixt. at atm. pressure and condensing the vapors.

Phenylglycine. C. J. STOSACKER. U. S. 1,442,743, Jan. 16. Aniline and chloroacetic acid are mixed in H_2O and after heating the mixt. sufficiently to initiate the reaction it is allowed to proceed without further heating to form the aniline salt of phenylglycine and aniline-HCl.

Glycols from chlorohydrins. G. O. CURME, JR. and C. O. YOUNG. U. S. 1,442,386, Jan. 16. A chlorohydrin, e. g., $\text{C}_2\text{H}_4(\text{OH})\text{Cl}$, is hydrolyzed with an alkali metal bicarbonate in soln. The evolved CO_2 , carrying entrained chlorohydrin, is led into a soln. of bicarbonate and the latter is later used for reaction with additional chlorohydrin.

p -Monoalkylaminophenylarsonic and -arsinic acids. C. J. ORCHSLIN. U. S. 1,440,621, Jan. 2. The corresponding base, e. g., amylaniline is allowed to react with

AsCl₃ in the presence of pyridine at a temp. of 100–120° and the product is oxidized with H₂O₂.

1,4-Dichloroanthraquinone- α -sulfonic acid. J. B. MARVIN, JR. U. S. 1,442,491, Jan. 16. Anthraquinone- α -sulfonic acid is treated with Cl under pressure in the presence of fuming H₂SO₄ to form 1,4-dichloroanthraquinone- α -sulfonic acid, which is sepd. from other reaction products by salting out and dissolving with alkali.

o-Sulfonic acids of aromatic amines. J. BADDILEY, J. B. PAYMAN and H. WIGNALL. U. S. 1,441,655, Jan. 9. Aniline, α -*m*-xylydine, β -naphthylamine or other aromatic amine is treated with chlorosulfonic acid in the presence of C₆H₅Cl₃ and the reaction mixt. is heated to complete the sulfonation and formation of *o*-sulfonic acid.

Thymol. M. PHILLIPS. U. S. 1,432,298, Oct. 17. Cymidinesulfonic acid is diazotized and the diazo product is reduced with NaHSO₃ soln. to cymylhydrazine-3- (or 5)-sulfonic acid, the hydrazine group is eliminated with FeCl₃ and the cymene-3-sulfonic acid obtained is converted into its Na salt and fused with NaOH or KOH to produce thymol. This pat. is dedicated for public use without royalty.

Reactive composition from "methyleamine-phenol" and a phenolalcohol. L. H. BAEKELAND. U. S. 1,442,420, Jan. 16. A sol. compn. which can be rendered insol. by further heating is formed from a "methyleamine-phenol" and a phenolalcohol, e. g., hexamethylenetetraminetriphenol and hydroxybenzyl alcohol.

11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

Pancreatic rennin. A. EPSTEIN. *Proc. Soc. Exptl. Biol. Med.* 19, 3-6(1921).—Fresh or well preserved dried preps. of pancreatic ext. ordinarily do not show any milk-coagulating enzyme. Rennin can be detected in solns. of the ext. after treatment in one of the following ways: (1) Heat the soln. at 50–65° for 10–15 min.; flocculation usually occurs, the enzyme remaining in soln. (2) Add suitable amts. of HCl. (3) Treat with precipitants such as colloidal iron, U acetate, alc., Na₂SO₄ and concd. CaCl₂. (4) Add products of peptic digestion, as gliadin or Witte's peptone. (5) Add serum of a rabbit immunized by intravenous injections of pancreatic exts. By these methods, some substance is pptd. which had previously concealed the presence of the rennin. Rennin is so far inseparable from trypsin, and combined they constitute about 1–2% of dry pancreatic ext. They may reside in a single chem. unit of the pancreatic substance and represent 2 phases of one and the same enzyme. The combined enzyme is of a protein nature, acid in character, coagulates at 82–5°, is extremely hygroscopic, and is not thrown down by the ordinary precipitants. It is active only in the presence of Ca, which must be available in ionizable form. Whether rennin exists in the pancreatic ext. as an active enzyme or as a pro-enzyme is discussed at some length; the evidence at present favors the former conception.

C. V. BAILEY

The effect of pancreatic rennet on blood coagulation. A. EPSTEIN and NATHAN ROSENTHAL. *Proc. Soc. Exptl. Biol. Med.* 19, 79-84(1921).—Purified pancreatic rennin-trypsin (cf. preceding abstract) was used. Controls of normal human blood showed a coagulation time of 11–12 min.; blood + 1% soln. CaCl₂ 5–8 min.; blood + rennin-trypsin 1–1.5 min.; blood + CaCl₂ soln. + rennin-trypsin 15–30 sec. The enzyme reduced the clotting time of the blood of a hemophiliac from 1.25 hrs. to 2 min. The time for citrated blood was reduced from 8 min. to 30 sec. Coagulation time varies

inversely with the amt. of enzyme. No untoward symptoms (anaphylaxis or intravenous clotting) followed the intravenous injection of large doses of purified rennin in rabbits; the effect of moderate doses on the clotting was not so striking as in the expts. *in vitro*; excessive doses increased the time after an initial shortening. C. V. B.

The effect of heat on the calcium salts and rennin coagulability of cow milk. L. S. PALMER. *Proc. Soc. Exptl. Biol. Med.* 19, 137-42(1921).—A colloidal suspension of CaHPO_4 was formed in a porcelain ball-mill by grinding first to a powder and then in the presence of 0.6% gelatin soln. After settling, the milky soln. contained 0.542 g. per 1000. Heating at 63° for 30 min. caused a heavy pptn. of CaHPO_4 , the aggregates passing, in part at least, into the crystalloid form. This explains the loss of CaHPO_4 when milk is pasteurized. Fresh whole milk, preserved by 1% toluene, was dialyzed in collodion bags for 48 hrs. Rennin added to this milk caused no coagulation in several hrs. A further addn. of 1 drop of 4 M CaCl_2 soln., or 2-3 drops of dil. HCl per 100 cc., caused instant clotting. The addn. of 10 cc. of the above soln. of gelatin and colloidal CaHPO_4 to 100 cc. of the rennin-treated milk caused no clotting, showing that this colloidal salt soln. plays no part in rennin coagulation. The chem. and physico-chem. reactions of rennin coagulation are briefly discussed. C. V. B.

Physiology of the surface of the cell. H. ZWAARDEMAKER. *Nederland. Tijdschr. Geneeskunde* 66, I, 2297-8(1922).—A general hypothesis concerning the structure of the surface of cell membranes involving conceptions of modern physical chemistry.

R. BRUYNER

Physical and chemical factors influencing the distribution of marine flora and fauna in the Strait of Georgia and adjacent waters. A. T. CAMERON AND (in part) IRENE MOUNCE. *Contrib. to Can. Biology* 1922, 41-70.—Temp., d., p_H , halide, carbonate, and a few Ca and Mg detns. have been made on surface and depth samples throughout the Strait of Georgia, B. C. These waters appear to be a true mixt. of ocean and Fraser River waters, with local variations due to small streams. The effect of the Fraser River decreases in winter; that of small streams increases. During the summer surface waters within the Strait become distinctly more alk.; the increase (max. p_H 8.85) is apparently due to increased temp. and admixt. with less saline waters changing the carbonate equil. Applications of the results are made to different types of localities. The conditions for Feb.-April in most parts of the Strait are not markedly different from those at points nearer the ocean. Therefore, early development of animal life will take place under approx. the same conditions. Growth, taking place during the summer, will be affected. Species requiring ocean conditions for optimum development may die, or develop poorly, or, if free-swimming, may find their correct habitat at a lower level, or even without the Strait. The same holds true for plants, and is evident in many cases; the luxuriance of algal growth is distinctly less in the less saline waters. The actual conditions at certain localities totally inhibit spore development where this takes place during the summer.

A. T. CAMERON

The oxygen content of waters in the Strait of Georgia. C. J. BERKELEY. *Contrib. to Can. Biology* 1922, 71-2.—By Winkler's procedure fairly concordant results were obtained, values of about 6 cc. O_2 per l. for surface waters steadily diminishing to 3.5 at 20 fathoms, and less than 2 cc. at 200 fathoms. The method, used with sea-water, involves an uncertain exptl. error of about 3%, which can be paralleled by addn. of Mg salts to tap-water, with which, alone, perfectly concordant results were found.

A. T. CAMERON

The relative chlorine, bromine, and iodine content in the waters of the Strait of Georgia, B. C. A. T. CAMERON. *Contrib. to Can. Biology* 1922, 75-80.—Winkler's methods for Br and I detns. (C. A. 10, 867, 1491, 2674) were used; total halide was detd. gravimetrically. The ratio Cl:Br:I was found to be 100:0.358:0.0002 as compared

with 100:0.347:0.00023 found by Winkler for the Adriatic. Most of the I was present as iodate (confirming Winkler). A. T. CAMERON

Colloidal chemistry and the study of enzymes. A. FODOR. *Kolloid-Z.* 31, 279-83 (1922).—A review of the important applications of colloidal chemistry in the study of enzymes. Before the kinetics of enzyme action can be thoroughly developed, it must be recognized that enzymes are colloidal in nature and surfaces involved will play an important role. Peptolytic enzymes when thrown down in fine suspension with protein are more active than when thrown down in coarse suspension. A further discussion is given of the relation of the grade of dispersion, elec. charge and the hydration of the colloidal particles in relation to enzyme action. A. A. CHRISTMAN

Colloidal chemistry and internal medicine. H. SCHADE. *Kolloid-Z.* 31, 283-7 (1922).—S. points out that colloidal chemistry can be an aid to the physician not only in the diagnosis of a disease but in its further study and cure. Colloidal methods are now used to test for abnormalities in body fluids. The nearer the correlation between cell function and its colloidal nature the better the evaluation that can be made of the change of the cells under pathol. conditions. Some of the applications of colloidal methods to clinical methods in medicine are briefly discussed. A. A. CHRISTMAN

The physico-chemical theory of stimulation. P. LASAREV. *Naturwissenschaften* 10, 1123-8(1922).—A summary of the mathematical principles of stimulation already developed by L. (cf. *Arch. ges. Physiol. Pflügers* 135, 197(1910); 142, 235(1911); 150, 371(1913); 154, 464(1913); 155, 310(1914); *Z. Sinnesphysiol.* 48, 172(1913); *Bull. acad. sci. Russie* 491, 1283(1917); *C. A.* 16, 2877). C. C. DAVIS

The adsorption of urea by animal charcoal and suspension colloids and its combination with proteins. K. HARPUDER. *Z. ges. expil. Med.* 29, 208-23(1922).—Animal charcoal does not produce any change in surface tension of urea solns. Under certain circumstances urea unites with proteins. Organ exts. have but little power of combining with urea. E. B. FINE

Solubilities of the phosphatides. G. V. STUCKERT. *Anales asoc. quim. Argentina* 10, 115-31(1922).—Ox brains were reduced to a paste and dried *in vacuo* over H_2SO_4 at 35°, then extd. successively with Et_2O , $EtOH$, and Me_2CO . The various exts. and residues were then repeatedly extd. with the same solvents in various orders until a large number of final products were isolated. The various compds. have great influence upon the soly. of each other in the various solvents; probably they adsorb one another. In many cases a residue insol. in a given solvent would, after extn. by another solvent, yield a considerable amt. of ext. when again treated with the first solvent. The phosphatides and esterins cannot be sepd. in a state of purity by the use of neutral solvents. The lecithins obtained by fractional extn. are not chem. well defined. Five distinct lecithin fractions are distinguished. Diagrams are given showing the fractional sepn. of the different constituents of brain. L. E. GILSON

The products of the prolonged tryptic digestion of casein. S. FRÄNKEL AND K. GALIA. *Biochem. Z.* 134, 308-21(1922).—These further studies of the products of prolonged tryptic digestion of casein (*C. A.* 15, 3642; 16, 3910) showed that *l*-tyrosine is first changed to *d*-tyrosine and then to *d*-tyrosine anhydride. *l*-Tryptophan goes over to *d*-tryptophan anhydride. *d*-Tryptophan itself has not yet been isolated. *l*-Hydroxyproline goes over into the racemic form. NH_2 is split off from the asparagine and glutamic acid groups. Glycine is changed to methylamine by decarboxylase. Histidine apparently is changed into its anhydride. *d*-Valine partly goes over into the racemic form. The anhydrase does not act on this amino acid and is apparently confined to the cyclic amino acids in its workings. The possible relation of these changes to the Walden inversion is discussed. F. S. HAMMETT

Peptone fermentation. E. BAUR AND E. HERZFELD. *Biochem. Z.* 131, 382-5 (1922).—A few brief speculations on the results previously published (*C. A.* 15, 3852)

and the citation of Schlatter's paper (*C. A.* 17, 290) as refutation of Bau's criticism (*C. A.* 16, 574).

F. S. HAMMETT

Color analysis of urine. III. Urochrome. M. WEISS. *Biochem. Z.* 133, 331-49(1922).—There is no pigment in urine which can be designated as "urochrome" in the earlier meaning of the "normal yellow pigment." The so-called urochrome is not a primary constituent of urine, but arises secondarily by oxidation from urochromogen, a pigment source found in normal and pathol. urines. Urochromogen plays no dominant role among the urinary pigments which are distributed among different endogenous and also apparently exogenous pigments and chromogens. However, urochromogen is the cause of the Ehrlich diazo reaction. The negative diazo reaction of Ehrlich which was formerly attributed to urochrome was due either to a relatively too small concn. of urochromogen or interference by other urinary pigments. These latter produce yellowish or greenish colors which mask the rose color of the Ehrlich test. Urochromogen arises when tissue disintegration is increased. It may increase ten times or more over the normal amt. excreted. In such cases, urochromogen makes up a larger proportion of the urinary pigments. It goes over very easily on oxidation into strongly colored pigments in alk. soln. and under certain conditions into uromelanin. The uromelanin produced from the urochromogen fraction of the pigments always bears a const. relation to the Ehrlich reaction, both in normal and in pathol. urines. Both urochromogen and uromelanin contain S in org. combination.

F. S. HAMMETT

Nomenclature of autolytic enzymes. K. G. DERNBY. *Biochem. Z.* 133, 432-3(1922).—The following classification is proposed:

Name	Substrate	Products	Optimum activity
Primary proteases (pepsinases)	Native protein (not peptones)	Peptones	Acid
Secondary proteases (trypsinases)	Denaturated proteins and peptones	Amino acids or peptides	Alk. or neutral
Tertiary proteases (creptases)	Peptides	Amino acids	Alk. or neutral

F. S. HAMMETT

Heat inactivation of amylase and its relation to the hydrogen ion concentration. H. LÜERS AND P. LORINSER. *Biochem. Z.* 133, 487-92(1922).—A prepn. from green malt was used. The inactivation const. in acetate-buffered solns. is lowest at the optimal p_H (5.0) and increases markedly on either side of this value.

F. S. HAMMETT

The action of iodine on diastase. L. BERCZELLER AND J. FREUD. *Biochem. Z.* 133, 493-501(1922).—Salivary diastase is inactivated by I in KI soln. If after a time the I is removed by $Na_2S_2O_3$ diastase activity is again evident. The presence of starch tends to render this inactivation less complete. Other expts. demonstrated that acid hydrolysis of starch is retarded by I. Hence a double effect is obtained. The opinion is expressed that I plays a more general role than that of a negative catalyst in hydrolysis.

F. S. HAMMETT

The solubility of certain protein precipitates in alcohols. L. BERCZELLER. *Biochem. Z.* 133, 518-34(1922).—The expts. show that single pptd. proteins are sol. in alc. (particularly gelatin-sulfosalicylic acid). This soly. is in many cases greater than that of the proteins. The soly. is not dependent on the soly. in alc. of the pptg. agent. For instance, the tannin-protein ppts. are insol. in alc. The great differences in soly. of the various pptd. proteins are not related to their precipitability. Proteins pptd. by heat are but little more sol. in alc. than native proteins. The methods used can be employed in the prepn. of pure proteins and their more exact characterization

F. S. HAMMETT

Studies of liver catalase. P. RONA AND A. DAMBOVICEANU. *Biochem. Z.* **134**, 20-38(1922).—The optimum activity of liver catalase ranges rather widely around p_H 7.0; fair activity is observed even up to p_H 11, at which concn. it is markedly slowed. In const. H_2O_2 concn. the extent of reaction is dependent on the absolute amt. of catalase present. The course of the reaction differs according to the relative amts. of enzyme and H_2O_2 . It is monomol. during the splitting of the greater amt. of H_2O_2 and bimol. at later stages. The inhibitory action of chlorides on catalase activity can be almost if not quite prevented by small amts. of Na_2CO_3 which do not alter the p_H . Quinine, vucine, atoxyl, methylarsin oxide, Na arsenate and arsenite have no influence on the enzyme. F. S. HAMMETT

The action of calcium on the coagulation of milk by rennet. P. RONA AND E. GABBE. *Biochem. Z.* **134**, 39-75(1922).—The influence of Ca was studied by detg. the time of coagulation of milk dild. from 10 to 30 times to which rennet had been added, and $CaCl_2$ after enzyme activity had been allowed to proceed for different lengths of time. The p_H was regulated by acetate buffers. The course of the enzyme activity was followed by detg. the temp. at which the milk was coagulated. When the Ca content dildn. and p_H are regulated, the coagulation temp. is characteristic for a definite degree of enzymic transformation of casein into paracasein. If $CaCl_2$ is added at the beginning of the enzyme action the coagulation time is later the higher the Ca concn. of the mixt. Small amts. favor and large amts. retard the enzyme activity. When $CaCl_2$ is added during the enzyme action the time of coagulation is prolonged according to the time of addition and the concn. of the salt. This retardation occurs on the addition of the small amts. which if added at the beginning of the reaction act as stimulants. This effect of the later addition of $CaCl_2$ is attributed both to an inhibitory action on the enzyme and to an alteration of the precipitability of paracasein. The change of casein to paracasein is only complete from p_H 6.0 to 6.4 the pptn. optimum of paracasein. At higher p_H , coagulation occurs before the casein has been completely transformed into paracasein. F. S. HAMMETT

Gel formation in quinine and eucupine solutions. P. RONA AND M. TAKAYA. *Biochem. Z.* **134**, 97-107(1922).—When 1.5 cc. of a 1% quinine-HCl soln. is mixed with 3 cc. of a phosphate buffer mixt. of p_H 6.85 the soln. at first is water-clear. After 5 or 10 min. needle crystals appear. A slight shifting towards the acid side prevents gel formation. At still greater H-ion concns. in acetate buffer no crystals are formed. Eucupine solns. of 1% concn. show similar sensitivity to slight change in p_H on the acid side. The nature of the buffer is of importance for gelation occurs in acetate mixts. of p_H 7.5 to 6.5 and not in phosphate mixts. of p_H 7.7 to 5.9. The concn. of the eucupine is also of importance. Gel formation occurs first in 0.1% solns. The higher the concn. the higher the hydriion concn. allowable for gel formation. The length of time before gelation begins depends on the concn. of the eucupine, buffer and H-ion. Increase in H-ion concn. within the limits p_H 6.0-6.5 lessens the gelation time. At higher p_H (7.8) slowing occurs. When the p_H is above 6.8 the reaction time is lengthened with decreasing amts. of eucupine. The lower the buffer concn. the longer is the reaction time. The formation of the gel and its resolu. is a reversible process. F. S. HAMMETT

Ion antagonism. H. WASTL. *Biochem. Z.* **134**, 131-8(1922).—The effect of various ions on the time of appearance of I in the reaction between HIO_3 and H_2SO_3 was studied. The standard mixt. was 1 cc. of a 1% soln. of HIO_3 , 0.5 cc. H_2SO_3 (1:10) and 5 cc. of distd. H_2O or the salt soln. being studied. K salts were used throughout. The SO_4^{--} retards the reaction more than the Cl^- favors it. In mixts. of SO_4^{--} and Cl^- the inhibition of the former is completely blocked. The Br^- acts similarly to the Cl^- but to a more marked degree. The same is true of the I^- . Similar antagonisms

were found between the NO_3^- and the Cl^- , Br^- and I^- . Studies of the antagonism between the I^- , Cl^- and Br^- showed that the addn. of Cl^- to I^- and Br^- contg. solns. retards the reaction. The Cl^- effect is much less towards I^- than towards Br^- . If the I^- is increased the inhibition by Cl^- is not found. No particular antagonism between I^- and Br^- was observed. The results do not indicate a superposition or additive effect of the single ions, but an opposite reaction of much specificity.

F. S. HAMMETT

The behavior of soap solutions at different hydrogen-ion concentrations. A. JARISCH. *Biochem. Z.* 134 163-76(1922).—Studies with Na oleate, palmitate, stearate, myristate, lauristate, etc. The addn. of a regulator of physiol. reaction to such solns. caused hydrolysis, decrease of surface tension and foaming ability, and turbidity due to liberated fatty acid in highly disperse condition. When hydrolysis was brought about in buffer mixts. of p_H 4.5, the fatty acid had its max. stability and there was obtained water-clear, relatively stable hydrosols having the properties of negative suspension colloids. This sol is precipitable by H ions. The clear fatty acid hydrosol is completely protected from coagulation by gelatin and other proteins. Hence such sols as occur in the animal body are stable and the condition of soly. of the parenteral fatty acids is explained. The hydrolysis of the soaps presumably takes place to a greater extent in the body than *in vitro* because of adsorption. Hence there can be but little if any soaps in the tissues, and added soap must be immediately hydrolyzed.

F. S. HAMMETT

The behavior of neutral red in soap solution. A. JARISCH. *Biochem. Z.* 134, 178-9(1922).—Soap solns. and lecithin emulsions in weakly alk. solns. (p_H 8 to 10) redden neutral red. This is attributed to the formation of a highly disperse fatty acid-neutral red complex. Nile-blue sulfate acts similarly.

F. S. HAMMETT

The analysis of a volume curve of blood corpuscles in hypertonic solutions. R. EGE. *Biochem. Z.* 134, 234-8(1922).—A reply to Takei (cf. C. A. 16, 582).

F. S. HAMMETT

The influence of starch on pepsin digestion. A. FISCHER. *Biochem. Z.* 134, 360-2(1922).—No evidence was obtained which justified the opinion that peptic digestion is inhibited by the presence of starch. The expts. were done *in vitro* with various samples of starch using 0.5% pepsin soln., 2.5% blood albumin and 0.1% HCl.

F. S. HAMMETT

The activation of rennet zymogen. B. J. HOLWERDA. *Biochem. Z.* 134, 381-9(1922).—The rennet solns. contained 10% NaCl as preservative. The activation of the pro-enzyme is optimum at a p_H 5.1 to 5.3 at 37°. Recognition is made of the salt effect on the p_H measurements. These acidities eventually exert a deleterious action on the enzyme. It is, therefore, recommended that rennet solns. be kept at p_H from 5.3 to 6.3.

F. S. HAMMETT

The decomposition of tertiary α -amino acids by yeast. A contribution to the biochemical destruction of amino acids. K. KURONO. *Biochem. Z.* 134, 424-33(1922).—The break-down of tertiary amino acids through the stage of the α -ketonic acid is not possible since oxidative deamination can only give rise to a ketone. Fermentation of *dl*-methylpropyl- α -aminoacetic acid with yeast gave an optically active form of this tertiary amino acid and methylpropylcarbinol. Apparently methyl propyl ketone was asymmetrically reduced.

F. S. HAMMETT

Synthesis of two new leucines. K. KURONO. *Biochem. Z.* 134, 434-6(1922).—Methylpropyl- α -aminoacetic acid, m. 295°, and methylisopropyl- α -aminoacetic acid, m. 293°, were synthesized according to the method of Zelinsky and Stadnikoffs (*Ber.* 39, 1722(1906)).

F. S. HAMMETT

Catalytic destruction of carnosine in vitro. W. M. CLIFFORD. *Biochem. J.* 16, 792-9(1922); cf. *C. A.* 15, 3856; 16, 1457, 2941.—Expts. are recorded to show that muscle exts. contain a catalyst that destroys carnosine. One such expt. was as follows: 3-5 g. minced lean beef was weighed in test-tubes and 10 cc. water added. The tubes were plugged with cotton and placed in a water bath at 100°. At intervals of 1-4 days a tube was removed, the contents were made up to 95 cc. with distd. water and 5 cc. of 20% metaphosphoric acid added to ppt. proteins. The carnosine in the filtrate was estd. colorimetrically (see references cited above). The results showed a gradual falling off in the % of carnosine from 0.99 the first day to 0.33 on the 21st day. For the % of carnosine to fall to the same level 9-10 months is necessary at 0° as against 21 days with a temp. of 100°.

BENJAMIN HARROW

A new phosphoric ester produced by the action of yeast juice on hexoses. ROBT. ROBINSON. *Biochem. J.* 16, 809-24(1922).—When fructose or glucose is fermented by yeast juice in the presence of sol. phosphate there is formed, in addition to the hexose-diphosphoric acid that has already been described by several authors, a hexose-mono-phosphoric acid. The prepn. and properties of the latter are described in detail. To prep. both hexosephosphoric esters, juice prepd. from fresh pressed English mild ale yeast is mixed with fructose or glucose and warmed to 26° in a water bath. Na_2HPO_4 is added from time to time in such quantity as to produce the max. rate of evolution of CO_2 . Solid $\text{Ba}(\text{OAc})_2$ is dissolved in the reaction mixt., which is then rendered just alkaline to phenolphthalein with baryta, and treated with an equal vol. of alc. The Ba salts of the 2 hexosephosphoric acids and of any excess of free H_2PO_4 are thus pptd. together with the protein of the yeast juice. The ppt. is washed with 70% alc., treated with boiling abs. alcohol and allowed to remain in contact with the alc. overnight, thereby denaturing the protein. The Ba salts are dried in a current of warm air, and ground with 10 parts of cold water; this dissolves the mono- but scarcely any of the diphosphate. The residue is washed twice with small quantities of water and then extracted with 200 parts of water; this dissolves the diphosphate. Traces of mineral phosphate are pptd. by $\text{Mg}(\text{OAc})_2$, and the Pb salt of the hexosephosphoric acid is pptd. by $\text{Pb}(\text{OAc})_2$. This is filtered, washed, suspended in water, decomposed with H_2S , filtered, the excess H_2S removed from the filtrate by a current of air, and the soln. neutralized with NaOH . The pptn. of the Pb salt is repeated several times. To the first ext. contg. the monophosphate, basic Pb acetate is added and the Pb salt is treated as above. The Ba salt is again formed and is pptd. from its soln. by alc., filtered off, washed with abs. alc., dried, dissolved in 10 parts of water "to which 10% alc. is finally added." The filtered soln. is treated with $\text{Hg}(\text{OAc})_2$, allowed to stand for some hrs., filtered, the basic Pb salt repptd. from the filtrate and once more converted into the Ba salt. This is finally purified by repeatedly dissolving it in 10 percent alcohol, filtering and reprecip. with an equal vol. of alc. It is washed with abs. alc. and dried in a desiccator.

BENJAMIN HARROW

The heat regulating mechanism of the body. H. G. BARBOUR. *Physiol. Rev.* 1, 295-326(1921).—A review. Body temp. is regulated by water shifting, but under nerve control. The binding of water by carbohydrates and by colloids is considered.

E. R. LONG

Physiological oxidations. H. D. DAKIN. *Physiol. Rev.* 1, 394-420(1921).—A review. The participation of water at some stage is an apparent abs. necessity in almost every oxidation. Free O is not always essential. The glutathione of Hopkins plays a real part in cell dynamics. The distribution and mode of action of catalase are such that there is no evidence suggesting that it is directly concerned in oxidation. The theory of β -oxidation of fatty acids (Knoop) has held its own. The main path of normal glucose metabolism lies by way of lactic acid, and the conversion to lactic

acid involves intramol. rearrangement, not oxidation. Glycerlaldehyde or methylglyoxal or optically active hydrates of the latter substance are probably intermediate stages.

E. R. LONG

The origin of the electrical change in muscle. B. A. McSWINEY AND S. L. MUCKLOW. *J. Physiol.* 56, 397-403(1922).—It is concluded that the production of lactic acid is not the prime cause of the elec. change.

J. F. LYMAN

Chemical notes—general. I. Some ferruginous concretions. THOS. STEEL. *Proc. Linnean Soc. N. S. Wales* 47, 441-2(1922).—A description with analyses is given of ferruginous stalagmites and stalactites (Fairy Dell, Wentworth Falls, N. S. Wales), concretions on twigs, leaves and fruits due to the action of chalybite water (Cranky's Creek Falls, N. S. Wales), and of "devil's dice" which are pseudomorphs of pyrite (2-8 mm. faces) and are found loose among gravel in the bed of the Talga River, W. Australia. The floor of a small cave at the foot of Cranky's Creek Falls is coated with a deposit of *epsomite* ($MgSO_4 + H_2O$). At Point Danger a spathic mineral strongly resembling kidney Fe ore and scattered through porphyritic dolerite proved to be *siderite* of compn.: $FeCO_3$ 88.22, Fe_2O_3 6.53, $CaCO_3$ 2.40, $MgCO_3$ 2.50, SiO_2 0.40. II. Coral lime, Fiji. *Ibid* 442-3.—Fijians cleanse and bleach their hair by means of a paste of coral lime. An analysis is given. III. Shell of *Helix aspera*. *Ibid* 443.—In Australia the shells of *H. aspera* are notably smaller and thinner than under the more rigorous conditions of their native habitat. The compn. is: CaO 54.00, P_2O_5 0.04, CO_2 40.24, SiO_2 0.10, conchiolin (contg. N 0.45) 5.00, H_2O 0.62%; equiv. to $CaCO_3$ 91.45, $Ca_3P_2O_8$ 0.09, CaO in org. combination 2.74, SiO_2 0.10, conchiolin 5.00, H_2O 0.62%. IV. Urinary secretions of birds and reptiles. *Ibid* 443-4.—Analyses are given of the urine of the common fowl, ostrich, *Python variegata*, *Moloch horridus*, and *Varanus varius*. The secretion from *Moloch horridus* was in the form of beautiful glistening white crystals. V. Fruit of banana. *Ibid* 444-5.—The analytical results are sucrose 5.65, dextrose and levulose 18.64, total sugar 24.29 and water 71.64%. Leuscher records the presence of 0.95% dextrin, but S. did not find any. VI. "Milk" of unripe coconuts. *Ibid* 445.—Old analyses are given. VII. Oxalic acid in plants. *Ibid* 445-6.—Scott described (*Trans. Linnean Soc. London* 1804, p. 262) the crystn. of $H_2C_2O_4$ on the surface of a dried specimen of *Boletus sulfureus*. (Cf. Steel, *C. A.* 15, 4019).

A. P.-COUTURE

Analysis of some invertase preparations. H. v. EULER AND K. JOSEPHSON. *Svensk Kem. Tids.* 34, 74-81(1922).—Some invertase preps. were analyzed by micro-methods, including the use of a micro balance. From the tabulated results the following figures are min. and max.: ash 1.8, 3.7; carbohydrates 30, 70; N 5.0, 7.8; P 0.83, 1.73%. These figures do not necessarily belong to the enzyme preps. with greatest or least activity. The most active prepn. has the least N % and the next most active prepn. the greatest. The N/P ratio is fairly const. for the purer preps. The tests for pentosans with orcin were negative. Reference is made to some other data published elsewhere from which it is inferred that the smallest molar wt. is between 1000 and 2000, that probably 10 to 20 such mols. are polymerized, and that the av. yeast cell from which their best preps. were made contained 8.10^{-14} g. invertase.

A. R. ROSE

The manifold nature of the proteins. THOMAS BLACKADDER. *J. Am. Leather Chem. Assoc.* 18, 5-12(1923).—A semi-popular discussion.

J. A. WILSON

BRUNDAGE, ALBERT H. *Manual of Toxicology*. 13th Ed. revised. Brooklyn, N. Y.: Henry Harrison & Co. 444 pp. \$3.

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PETERSEN, WM. F. *Protein Therapy and Non-specific Resistance.* London: MacMillan. 21s.

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B—METHODS AND APPARATUS

STANLEY R. BENEDICT

The determination of chlorides in organs and foodstuffs. ST. RUSZNYÁK AND D. KELLNER. *Biochem. Z.* 133, 350-4(1922).—For the macro-method of Cl detn. 2-5 g. of the material, according to its Cl concn., is dried, not only for the detn. of the % H₂O but to avoid dünn. of the HNO₃ used in oxidation. The dried material is heated with Cl-free concd. HNO₃ (1.5 to 3 cc. HNO₃ for each g. of substance) until completely disintegrated. This can be hastened by shaking. The soln. is dild. with H₂O and the requisite amt. of 0.01 or 0.1 N AgNO₃ added. The mixt. is heated again and KMnO₄ crystals are added until the brownish discoloration remains permanent. Decolorization with glucose is next effected, the soln. is cooled and the excess AgNO₃ detd. by titration with NH₄CNS Fe-alum as indicator being used. The concn. of the NH₄CNS soln. used depends on the strength of the added AgNO₃. This process does not completely get rid of fat, but no disturbance is produced thereby. The micro-method is merely an adaptation of the above with smaller amts. of material and 0.01 N AgNO₃. A list is given of the Cl content of liver, muscle, skin, kidneys, spleen, etc., from various animals and of various foodstuffs.

F. S. HAMMETT

Rearrangement of the Plesch chromophotometer into a nephelometer. ST. RUSZNYÁK. *Biochem. Z.* 133, 365-9(1922).

F. S. HAMMETT

Nephelometric determination of the albumin-globulin quotient. ST. RUSZNYÁK. *Biochem. Z.* 133, 370-2(1922).—0.1 cc. of serum is measured into each of 2 Erlenmeyer flasks. To one flask there is added with continuous rotation 25 cc. of a half satd. (NH₄)₂SO₄ soln. (globulin); to the other flask 50 cc. of the half satd. (NH₄)₂SO₄ soln. made acid to 0.1 N with HCl (total protein). The 2 solns. are compared in the nephelometer after a few min. The ratio between total protein and globulin is multiplied by 1.996. The subtraction of unity (1) from this ratio gives the albumin-globulin ratio. The results obtained by this method are in good agreement with those obtained gravimetrically.

F. S. HAMMETT

Methods for the chemical study of blood. V. Blood sugar determination. A. ROSENTHAL. *Biochem. Z.* 133, 469-75(1922).—After a critique of various methods for sugar detn. R. proposes the following scheme. 1 cc. of blood, plasma or serum is deproteinized as usual with metaphosphoric acid or Na tungstate and the ppt. washed so that the filtrate amts. to 100 cc. This is treated with 5 cc. of K₃Fe(CN)₆ soln. and heated for exactly 3 min. at 75-85° by a current of steam. After cooling, 5 cc. of KI soln. is added, with a few drops of AcOH and of a 1% starch soln. as indicator. After standing for a few min. the mixt. is titrated with 0.005 N Na₂S₂O₄. A table giving the amt. of sugar in mg. equiv. to the K₃Fe(CN)₆ used is given. The K₃Fe(CN)₆ soln. contains 1.6400 g. of the salt and 10.6 g. Na₂CO₃ per l. The KI soln. contains 5 g. KI, 10 g. ZnSO₄ dissolved in 200 cc. H₂O and 50 g. NaCl. The detn. should be made immediately after the blood sample is taken.

F. S. HAMMETT

A rapid method for the exact determination of small amounts of uric acid in urine and blood serum. H. CHANTRAINE. *Biochem. Z.* 133, 605-12(1922).—C. was unable to find a method for the detn. of small amts. of uric acid. Since his method requires some 100 cc. of serum and depends on the isolation of uric acid in the pure state and its oxidation by KMnO_4 soln. the details need hardly be given in view of the more satisfactory colorimetric methods now in common use.

F. S. HAMMETT

A new reaction of blood. G. BECCADELLI. *Biochem. Z.* 134, 180-2(1922).—0.5 cc. blood or serum is mixed with 0.5 cc. HCHO (38 to 40%), 0.5 cc. AgNO_3 (0.75%) and NH_4OH (0.925%) in the order given. In 3 or 4 min. the blood takes on a color characteristic for its origin. Human blood gives an amber nuance, other animals different yellows. The depth of color is dependent on the age of the blood stain, when such is used. Instead of coloration, *syphilitic blood* shows decolorization. In the test the serum is obtained by sedimentation; it must be clear and not inactivated.

F. S. H.

The pharmacological and colorimetric determination of adrenaline in pure and decomposed solutions and adrenal extracts. H. MARWEG. *Biochem. Z.* 134, 292-300 (1922).—Folin's method for the detn. of adrenaline gives too high values for solns. in which the compd. is partially decompd. Very inexact values are apparently given by the colorimetric method when applied to adrenal exts. The content in adrenaline precursors gives rise to too high values. The pharmacol. activity of adrenaline is not enhanced by oxidative decompn.

F. S. HAMMETT

A simple method for obtaining a dry urease preparation; its activity and properties. G. REVOLTELLA. *Biochem. Z.* 134, 336-48(1922).—200 g. of finely powd. soy-bean meal is allowed to stand for 5 or 6 hrs. in 1 l. of H_2O . The supernatant liquid is filtered off with suction and treated with 96% alc. until pptn. is complete. About 400 cc. alc. is necessary. The pptd. protein is centrifuged out, spread thin and dried until, when gradually mixed with 80 g. of lactose, it has a doughy consistency and does not stick to the container. It is then rapidly dried in a current of air, weighed and sufficient lactose added to make the total wt. 100 g. The dust-free enzyme mixt. is then put in a bottle and kept dry. Studies with this prepn. showed it to be as active as other preps. and but slightly affected by room temp. and light. The advantages of such a dry prepn. are obvious.

F. S. HAMMETT

Method for the determination of amino acids and ammonia using a control distillation apparatus. G. REVOLTELLA. *Biochem. Z.* 134, 349-53(1922).—Description of a distn. app. for use in freeing urine from NH_3 so that the amino acids can be easily titrated according to Sørensen.

F. S. HAMMETT

Determination of p_{H} of microscopic bodies. G. F. A. PANTIN. *Nature* 111, 81(1923).—Neutral red may be used as an intra-vitam stain and is also a fairly good indicator. If, therefore, cells are stained with neutral red, the color of the stain as observed with the microscope gives one a rough indication of the p_{H} within the cell. A series of tubes contg. solns. of increasing p_{H} is made up in the ordinary way, and a few drops of neutral red are added. Holes are cut, at intervals, in a stout cardboard strip and the tubes inserted (the tubes should fit tightly). The strip with the tubes hanging freely below it is now suspended in the window. With the aid of the microscope condenser the series is focussed sharply in the plane of the object which is being examd. The appearance down the microscope now consists of the stained object and by its side the image of the series of tubes. By tilting the mirror the images of successive tubes of different p_{H} can be brought into juxtaposition with the object examd. In this way the p_{H} of the stained body can be detd. by direct comparison.

BENJAMIN HARROW

The determination of blood catalase, with some observations on the factors affecting the ratio between quantity and activity of this enzyme. RUTH OKEY. *Am. J.*

Physiol. 62, 417-37(1922).—Catalase activity was detd. from the amt. of H_2O_2 *undecompd.* after interaction, under standard conditions, between enzyme material and a measured amt. of H_2O_2 . H_2O_2 was detd. by titration with $KMnO_4$ in acid soln., the $KMnO_4$ acting as an oxidizing agent and mol. O_2 being evolved. The effects of temp., previous heating of the enzyme material to 55° , and the presence of preservatives on the catalase reaction were studied. Comparatively small day to day and hour to hour variations in temp. may be sufficient to account for many smaller variations in catalase content reported by previous workers. Detns. of catalase must be made under much more carefully controlled conditions than in the past if they are to be of value.

J. F. LYMAN

The preservation of salivary amylase with glycerol. E. DOUMER. *Compt. rend. soc. biol.* 87, 678-9(1922).—Human saliva dild. with an equal vol. of distd. water was preserved with glycerol. Samples of this were tested from time to time in the course of several years for its amylolytic activity, which was found to be unaltered. It is well to note that no special precaution was taken as to the manner of preservation as the tubes were kept at various temps.

S. MORGULIS

Chronometric determination of iodine in the urine. E. RIEGLER. *Compt. rend. soc. biol.* 87, 793-4(1922).—To 10 cc. of urine dild. 1:10 in a test tube are added 5 drops of 25% H_2SO_4 , 5 drops of 2% $NaNO_2$ and 5 drops of a 1% starch soln. The tube is stoppered and the contents are mixed by inverting the tube several times, then 1 cc. of ethyl acetate is added and the chronometer is started at the same moment. The stoppered tube is carefully inverted about 10 times while the discoloration proceeds. The amt. of I_2 in mg. present in the urine is calcd. from the formula $P = T/5$, where T is the time in secs. required.

S. MORGULIS

Determination of serine and of carbon dioxide-globulin in serum. A rapid and sufficiently exact procedure. F. DEMYTTENARE and A. BESSEMANS. *Compt. rend. soc. biol.* 87, 800-2(1922).—Serum is dild. 1 part with 9 parts of water, and in this the dry residue is detd. The soln. is then satd. with CO_2 and is centrifuged. The dry residue is then again detd. in the remaining soln. The analysis is actually carried out as follows: 3.5 cc. serum is dild. with 31.5 cc. H_2O . 10 cc. of the mixt. is evapd. in a weighed crucible to const. wt. This gives the dry residue in 1 cc. serum (A). 20 cc. is now treated with CO_2 and, after centrifuging, 10 cc. is evapd. (B) and the difference in wt. between A and B gives the amt. of CO_2 -globulin per cc. of serum. The first dry residue (A) is now mixed with 10 cc. of 0.1 N H_2SO_4 , dried and incinerated. The residue represents Na_2SO_4 and by multiplying the wt. by 0.8239 the wt. of NaCl is found (C). $A - C =$ the total proteins, and $B - C =$ serine in 1 cc. of serum.

S. MORGULIS

Determination of potassium in the blood. D. OLMER, L. PAYAN and J. BERTHIER. *Compt. rend. soc. biol.* 87, 865-7(1922).—The blood is deproteinized with CCl_3CO_2H . A vol. corresponding to 10 cc. of serum is taken and is evapd. with 2 cc. of a 1% Na_2CO_3 soln. (free from K) in a crucible, to remove any NH_3 . The vol. is reduced to about 2-3 cc. when it is acidified with 3 drops of HCl and mixed with 0.5-1 cc. of a 10% aq. soln. of $PtCl_4$. This is then evapd. just to dryness and, when cool, treated with about 10 cc. acetone. The ppt. is carefully ground in the crucible and after 20 min. is filtered off, washed several times with acetone and finally with ether. The residue on the filter is now dissolved in 20 cc. boiling water. To this soln. is added 1 cc. of 10% Na_2CO_3 and 0.5 cc. of 10% formalin, and after boiling a few min. the K_2PtCl_6 is decompd. with the liberation of Pt and KCl. After filtering the material either the Pt or the Cl is detd. and from this the KCl content of 10 cc. serum calcd.

S. MORGULIS

Determination of iodine in thyroid extracts. RENE FABRE and HENRI PÉNAU. *Compt. rend. soc. biol.* 87, 1026-8(1922).—1.1 g. of thyroid ext. is transferred to a Ni crucible and mixed with 4 cc. alc. and 5 cc. of 20% KOH. This is left for 3-4 hrs.,

being stirred with a Ni spatula; the alc. is then carefully driven off by warming on a water bath and the residue is ignited over an alc. lamp. To destroy all the carbonaceous matter it is necessary to take up the material again in a little water, evap. and repeat the ignition over the alc. flame with the usual precautions against loss. The residue is at last dissolved in hot 0.2% NaCl soln. and the crucible boiled several times with the salt soln. until the final vol. is 200 cc. (filtered). This is now mixed with 10 cc. of 2% KMnO_4 and boiled for 10 min. in an Erlenmeyer flask. By this operation the iodides are transformed into iodates, and a slight excess of KMnO_4 should remain. This is then removed by boiling with a little alc. and after cooling the mixt. is made up to 220 cc. in a vol. flask. To 200 cc. are added 10 cc. of pure AcOH and 1 g. NH_4Cl and the mixt. is boiled again to destroy the nitrites. To the hot soln. are added another 10 cc. of AcOH and 1 g. of KI . After allowing this to stand five min. the liberated I is titrated with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$. The quantity of I is calcd. from the formula (where n is the number of cc. used in titration): $\% \text{I} = n \times 0.00127 \times 100/6$.

S. MORGULIS

Determination of urotropine. Studies on the decomposition in vitro in blood. P. GÉRARD AND S. MOISSONNIER. *Compt. rend. soc. biol.* **87**, 1073-5(1922).—The hydrolysis of urotropine by acid into NH_3 and HCHO is the basis for the detn. The blood is deproteinized with an equal vol. of CCl_3COOH (20%) and to the filtrate is added 1 cc. of concd. HCl and the whole heated $1/2$ hr. in the water bath. The acid is now neutralized and the NH_3 detd. by Folin's aeration method. By this method 96-98% of the urotropine could be recovered. 100 cc. of blood was divided into 4 samples to 2 of which a measured amt. of urotropine was added (0.5 g. per 100 cc.). The other 2 served as controls. One set was kept for 24 hrs. at room temp. and another at 37° . The decompn. of the urotropine *in vitro* was practically nil. S. MORGULIS

Studies on hemoglobin. I. The advantage of alkaline solutions for colorimetric determination of hemoglobin. HSIEN WU. *J. Biochem. (Japan)* **2**, 173-80(1922).—Variations in protein and in lipid form an important source of error in the detns. of hemoglobin by the acid hematin, methemoglobin or cyanohemoglobin methods. A new procedure is suggested based on the use of either ammoniacal methemoglobin or cyanohemoglobin and of alk. hematin which overcomes these objections. An alk. hematin soln. is prepd. readily by making an acid hematin soln. alk. by this simple method: Dil. 1 cc. of blood in a 100 cc. flask with 80 cc. H_2O ; add to this 1 cc. of concd. HCl and allow to stand about 40 min. for the acid hematin to form. Then add 10 cc. of 10% NaOH , make up to vol. and mix. This soln. does not keep well and should be prepd. fresh. It can be made from a stock standard soln. in this way. A 10% soln. of blood or a corresponding soln. of pure hemoglobin preserved with 4% NaF keeps at least a month at ordinary temp. The stock is made by measuring into a 1 l. vol. flask 100 cc. of blood the hemoglobin content of which has been detd. by the O_2 capacity method. Add to this 800 cc. of H_2O in which 40 g. NaF has been dissolved. Make up to vol. and filter.

S. MORGULIS

The determination of albumin by nephelometric method. HENRI BENARD AND ALBERT LABORDE. *Compt. rend.* **176**, 98-101(1923).—The value of the nephelometric method of B. and L. (*Compt. rend. soc. biol.* **22**, 602), based on the detn. of the intensity of the Tyndall phenomenon, and that of Cheneveau and Audubert (*C. A.* **14**, 1621) are compared. Up to 1.5 of albumin per 1000 the opacity obtained by the method of Cheneveau and Audubert is a straight-line function of the concn.; at higher concns. the relation is complicated. The B. and L. method gives a straight-line function only up to 0.8 albumin per 1000. The optical properties of the solns. depend on the concn. of CCl_3COOH or sulfosalicylic acid used for pptn., probably because of varying degrees of aggregation of the proteins. The C. and A. method is preferable in case of rapid settling of the suspension.

BENJAMIN S. NEWHAUSEN

Quantitative determination of glucose and lactose in blood and urine. WM. THALHIMER AND MARGARET C. PERRY. *J. Am. Med. Assoc.* 79, 1506-8(1922).—The objections to the methods in use for detg. mixts. of glucose and lactose in the same soln. are reviewed and the following new method is proposed: The total sugar is first detd. as glucose by the Folin-Wu blood sugar method for blood or serous fluids, and by the recent Folin-Berglund method for sugar in urine for urines. The soln. is then heavily inoculated with *B. paratyphosus* B from a 24-hr. growth on an agar slant, and is incubated 48 hrs. The amt. of sugar remaining is then detd. by the appropriate method. If no reducing substance is left, only glucose is present. If there is still a reducing substance, this is detd. as lactose. The strain of *B. paratyphosus* B used in this study was obtained from the collection of type cultures maintained at the Army Medical Museum by the Soc. Am. Bacteriologists. Sterile solns. for inoculation with *B. paratyphosus* B were obtained by autoclaving at 15 lbs. for 15 min. Sugar detns. before and after autoclaving of weak solns. showed no loss of sugar. Contaminated urine was sterilized by filtering through a Mandler filter without loss of sugar. Since the sugar-splitting ability of *B. paratyphosus* B is limited, preliminary sugar detns. of the unknown specimens should be made and if necessary the concn. of the sugar should be reduced before inoculation to about 0.3%. The use of the selective action of various types of bacteria for different carbohydrates offers a means of more completely detg. the substances which constitute the reducing material in normal and in abnormal urine.

L. W. RIGGS

Determination of small amounts of Mg (HAMMETT, ADAMS) 7.

BANG, IVAR. *Mikromethoden zur Blutuntersuchung*. 3rd Ed. München and Weisbaden: J. F. Bergmann. 48 pp. M 24.

CUMMER, CLYDE L. *Manual of Clinical Laboratory Methods*. London: H. Kimp-ton. 484 pp. 28 s. Reviewed in *Nature* 110, 731(1922).

HADEN, RUSSEL L. *Clinical laboratory methods*. St. Louis: The C. V. Mosby Co. 294 pp. \$3.75.

Handbuch der biologischen Arbeitsmethoden. Chemische Methoden. Spezielle analyt. u. synthet. Methoden. Kohlenhydrate. Allg. u. spezielle Methoden zu ihrem Nachweis in qualitativer u. quantitativer Beziehung.—Ihre Isolierung.—Aufbau u. Abbauprodukte, GEZA ZEMBLÉN. 400 pp. M 120. Chemische Methoden. Spezielle analyt. u. synthet. Methoden. Phosphatide, Fette, Sterine. Allgemeine Methoden zum Nachweis, zur Darstellung und zur Bestimmung d. Lipoide, einschliesslich d. Cholesterins d. tier. Organismus, SIGMUND FRÄNKEL. Darstellung von Phosphatiden aus Pflanzen, ERNST WINTERSTEIN. Cerebroside, HANS THIERPFELDER. Abbau- und Aufbauversuche im Gebiete d. Sterine, A. WINDAUS. Darstellung d. Gallensäuren u. ihre wichtigsten Abbauprodukte u. ihr Nachweis, OLAF HAMMERSTEIN. Methoden d. Abbau- und Aufbauversuche auf d. Gebiete d. Gallensäuren, W. BORSCHKE. 284 pp. M 84. Besondere Methoden zum Nachweis d. einzelnen Aminosäuren, ARTHUR WEIL. Die Analyse von Eiweisskörpern durch Bestimmung d. chemische-charakterist. Gruppen d. verschiedenen Aminosäuren, D. D. VAN SLYKE. Isolierung von Aminosäuren, Asparagin, Glutamin usw. aus Pflanzen, ERNST WINTERSTEIN. Nachweis, Bestimmung u. Synthese d. Monoaminosäuren, ANDOR FODOR. Methoden zur biol. Spaltung racemischer Aminosäuren durch lebende Organismen, FELIX EHRLICH. Isolierung, Bestimmung u. Nachweis von Histidin, Lysin u. Arginin (Ornithin u. Guaniden). Synthese u. Abbau d. Hexonbasen, HERMANN STEUDEL. Darstellung d. Carbinaminosäuren, H. ZIMMERMANN. Die Formoltitration, HANS JESSEN-HANSEN. 262 pp. M 78. Chemische Methoden. Eiweissstoffe—Einfache Eiweisskörper. Proteine. Histone u. Protamine, HERMANN STEUDEL. Das Arbeiten mit Organeleiweiss, JULIUS POHL. Darstellung u. Untersuchung e. wohldefinierten Eiweissstoffes, HANS JESSEN-

HANSEN. Umwandlungsprodukte d. Proteine, EDUARD STRAUSS. **Methoden zur Eateiweissung von eiweisshaltigen Flüssigkeiten**, PETER RONA AND EDUARD STRAUSS. **Tierische Pigmente u. Farbstoffe**, FRANZ SAMUELY AND EDUARD STRAUSS. 577-800 pp. M 75. **Methoden zur Erforschung d. Leistungen, d. Pflanzenorganismus. Spezielle Methoden. Methodik zur Beeinflussung d. Samenkeimung u. d. Wachstums von Keimpflanzen**, VIKTOR GRAFE. **Methoden zum Studium d. Wachstums d. Pflanzen u. seiner Beeinflussung**, V. VOUK. **Methoden d. Frühtreibens von Pflanzen**, FREIDL, WEBER-GRAZ. **Das Sterilisieren höherer lebender Pflanzen**, VIKTOR GRAFE. **Methoden d. Sand u. Wasserkultur höherer Pflanzen**, ERNST G. PRINGSHEIM. 445-654 pp. M 60. Edited by E. Abderhalden. Berlin and Vienna: Urban und Schwarzenberg.

C—BACTERIOLOGY

A. K. BALLS

Internal disinfection. In vitro experiments with acridine dyes. P. WELS. *Z. ges. expul. Med.* 28, 347-37(1922).—Concd. dye solns. increase the natural bactericidal action of serum. This increase is proportional to the increased concn. of dye in the serum. In certain circumstances weak dye solns. decrease the bactericidal power of serum. The addition of small pieces of tissue decreases the bactericidal power of serum-dye solns.

E. B. FINK

The inhibitory action exerted by copper compounds and glass on the development of bacteria. G. VON LINDEN. *Centr. Bakt. Parasitenk. I Abt.* 87, 310-5(1921); *Chimie & Industrie* 8, 569(1922); cf. *C. A.* 15, 3144.—Glass which has contained Cu compds. retains, even after several washings bactericidal power. This is ascribed to adsorption, and formation of slightly sol. CuSiO_3 .

JACK J. HINMAN, JR.

The biochemical differentiation of bacteria. H. W. SMITH. *Am. J. Hyg.* 2, 607-55(1922).—On the bases of Gram reaction, optimum p_H , strong electrolytes, weak electrolytes, nonelectrolytes, NaOH lysis, tryptic digestion, and sporulation, bacteria were divided into 2 great groups. This division of bacteria is said to accord nicely with the sepn. of bacteria into families, genera, etc. 102 references are appended.

F. W. TANNER

GRAVES, JO. HAMES. **Agricultural Bacteriology.** Philadelphia: Lea & Febiger. 437 pp. \$4.

PARTIDGE, WM. **Aids to Bacteriology.** 4th Ed. New York: Wm. Wood & Co. 276 pp. \$1.75. Reviewed in *J. Am. Med. Assoc.* 79, 2107(1922).

ZINSSER, HANS AND ZINSSER, A. **A Textbook of Bacteriology.** 5th ed. revised New York: Appleton. 1193 pp. \$7.50.

D—BOTANY

B. M. DUGGAR

Suction pressure of the plant cell. A note on nomenclature. WALTER STILES. *Biochem. J.* 16, 727-728(1922).—In addn. to the osmotic pressure tending to send water into the cell (assuming the system immersed is in water), there develops a hydrostatic pressure and consequent stretching of the wall, which, being elastic, exerts an inwardly directed pressure on the cell contents. The hydrostatic pressure of the water in the cell (turgor pressure) is equal and opposite to the inwardly directed wall pressure. If this pressure be called T and the osmotic pressure P , the net pressure sending water into the cell when this is surrounded by water is $P-T$. S. proposes the term "suction pressure" to denote the actual pressure sending water into the cell when this is immersed in pure water.

BENJAMIN HARROW

Transport of organic substances in plants. H. H. DIXON. *Nature* 110, 547 (1922).—The transport of org. substances needed in the distal growing regions is effected through the tracheae of the wood. The substances travel dissolved in the water, following these channels, which is moved by transpiration, expansion of the growing cells, or root pressure. Physical considerations make it impossible to admit that sufficiently rapid transport can be afforded by the bast either for the observed upward or downward distribution of org. substances. The existence of downward as well as upward movement of water in the tracheae of the wood may be demonstrated, and may be inferred by transport of "hormones" in the wood. BENJAMIN HARROW

The availability of mineral plant food (a modification of the present hypothesis). N. M. COMBER. *J. Agr. Sci.* 12, 363-9 (1922).—After presenting the present hypothesis and discussing its inadequacy, C. presents a modification of the hypothesis. He bases his modification upon the absorption of colloids by the plant reasoning therefrom that constituents of the soil may, as colloidal gels, enter the plant. He takes exception to the number of elements which are usually considered as essential to plant growth (listed as ten) based upon the fact that the mechanism of plant feeding in soil is different from that promoting plant growth in water soln. He offers this as an explanation of the presence of other elements often found in soil-grown plants. These ideas are further elaborated in considering the relation of the root hairs to the soil particles and the chem. possibilities of the union of the plant and the soil. R. B. DEEMER

Presence of aucubin in seeds of *Veronica hederifolia* L. C. CHARAUX. *Bull. soc. chim. biol.* 4, 568-70 (1922).—The glucoside extd. from these seeds is identical with that in *Aucuba* and other genera. A. T. CAMERON

A glucosidase from *Dimorphotheca ecklonis*, D. C. L. ROSENTHALER. *Fermentforschung* 6, 197-9 (1922).—This S. African member of the Compositae contains a glucoside which is identical with linamarin or phaseolunatin; it can be split into HNC, glucose and acetone (*C. A.* 16, 2387). This cleavage takes place when the plant is covered with water, and depends on an enzyme which can be pptd. with alc. This is called linamarase, and as it is injured by alc. more active preps. are obtained by pptn. with $MgSO_4$ or $(NH_4)_2SO_4$. It does not hydrolyze α -methylglucoside or maltose, and has little if any action on salicin and amygdalin. H. G. WELLS

Variability statistics as a help in the study of plant biochemistry. L. ROSENTHALER. *Biochem. Z.* 134, 225-33 (1922).—Simple comparisons are made showing the existence of a relationship between HCN-N and total N in seeds and leaves and the implications therefrom; also showing the relation between the caffeine and protein N of cola seeds. F. S. HAMMETT

Enzyme formation in germinating seeds. A. BACH AND A. OPARIN. *Biochem. Z.* 134, 183-9 (1922).—The formation of enzymes in the germinating seeds of sunflower and corn was followed by methods which showed the activity of catalase, peroxidase, oxygenase, amylase and protease. The 3 former are present in greater amt. at all times than the 2 latter. The enzyme content rises to a max. during germination and then falls. The catalase of corn reaches its max. in 3 or 4 days; the other enzymes not until 6 or 8 days have passed. The max. value of all the enzymes of sunflower seeds is reached in the 6th or 7th day of germination. The catalase content of germinating sunflower seeds is greater than that of corn. The content in the other enzymes is less. The addition of $CaCO_3$ to the rest of the growing corn before extn. causes a great increase in catalase activity. F. S. HAMMETT

Influence of oxygen on the enzyme formation in germinating corn. A. OPARIN. *Biochem. Z.* 134, 190-3 (1922).—An increase in the partial pressure of O_2 has no influence on the enzyme formation with the exception of oxygenase, the formation of which was markedly decreased in an atm. of pure O_2 . The replacement of O_2 by an inert gas re-

tards enzyme formation at all stages of germination. Oxygenase is an exception.

F. S. HAMMETT

Cell respiration. I. Respiration of yeast cells. P. RONA AND K. GRASSHEIM. *Biochem. Z.* **134**, 146-162(1922).—CO₂ output of yeast (*Torula pulcherrima*) was detd. under various conditions. The optimum activity lay in a wide but sharply limited range of pH 4.5-6.6. On either side of these values respiration drops off rapidly. In both phosphate and acetate buffers the same effect is shown. The age of the yeast is a factor in the extent of respiration. When the culture is 2-7 days old optimum activity is evident. Then it decreases rapidly and is completely gone by 14 days. O₂ consumption is some 30% less in phosphate-buffered mixts. than in acetate. The concn. of the buffer soln. is not a matter of indifference. In phosphate mixts. a 1/3 mol. concn. is the best. If the yeast cells are injured by repeated freezing and thawing the extent of respiration and the hydron activity are not affected; the optimum remains in the same range.

F. S. HAMMETT

Stimulation of plants by carbon disulfide. CARRIE OLDENBUSCH. *Bull. Torrey Bot. Club* **49**, 375-89(1922).—Expts. were made on (1) wheat grains (*Triticum sativum*) and *Vicia faba* seedlings, (2) buds of willow trees and (3) spores of *Rhizopus nigricans* and *Sterigmatocystis nigra* in hanging drop cells. The av. growth is recorded in microns for 10 germination tubes of the fungous spores inoculated on nutrient media to which CS₂ was added. The dry wts. of cultures of the last named fungus are recorded in mg. CS₂ acts on plants as many other chemicals do. In concd. aq. solns. or as vapor for too long a time it inhibits growth; in dil. solns. or as vapor for a short time it stimulates dormant protoplasm, active protoplasm and the conidial spores of certain fungi. 0.00005 M solns. gave considerable stimulation to active protoplasm and solns. 3 or 4 times as strong stimulated dormant protoplasm. As is the case with other stimulants the acceleration of growth lasted but a short time and was followed by normal growth.

F. C. COOK

Resistance of leaves to asphyxia. L. MAQUENNE AND E. DEMOUSSY. *Bull. soc. chim. biol.* **4**, 571-6(1922); cf. *C. A.* **16**, 273.—Soft leaves (bean, dahlia, sugar beet, geranium) kept in CO₂ survive only some days, gooseberry leaves only 24 hrs. In willow and cherry leaves chlorophyll shows signs of alteration after 5 or 6 months. Leaves of the *Aucuba* survive over a year; the chlorophyll still functions. Decompn. of CO₂ during the day provides the O₂ necessary for life. Those leaves which die quickly have only a slight degree of internal respiration and during the latter part of each night are therefore in a state of complete asphyxiation.

A. T. CAMERON

Soil acidity—its nature, measurement and relation to plant distribution (WHERRY)

15. Natural and artificial pepper substances (ORR, *et al.*) 10. Cork substance (KARRER, *et al.*) 10.

WRANGELL, M. VON. *Gesetzmässigkeiten bei der Phosphorsäuerernährung der Pflanze.* Berlin: P. Parey. M 25.

E—NUTRITION

PHILIP B. HAWK

NORMAL

Some common Korean foods. J. D. VAN BUSKIRK. *Publication No. 25 Severance Medical College, Seoul.*—A study of Korean diet, with recommendations.

WM. H. ADOLPH

The existence of a hitherto unrecognized dietary factor essential for reproduction. HERBERT M. EVANS AND K. S. BISHOP. *Science* **56**, 650-1(1922).—Rats raised on a

dietary consisting of purified protein, fat and carbohydrate to which adequate salts and vitamins were added to assure normal growth were sterile; fertility was restored on the feeding of lettuce. Butter fat may contain a small amt. of the substance *X*, responsible for fertility but the authors consider it distinct from fat-sol. A since some diets which cause eye involvement (lack of fat-sol. A) are apparently without effect on fertility. From similar expts. the authors consider *X* to be distinct from water-sol. B and C.

A. A. CHRISTMAN

The importance of certain fat-free nutritive substances for the growth and maintenance of the animal organism. WILHELM STEPP. *Naturwissenschaften* 11, 33-7 (1923).—A review of work on vitamins.

C. C. DAVIS

How the vitamins act. ANTONIO DE GREGORIO ROCASOLANO. *Anales soc. españ. fis. quim.* 20, 433-6(1922).—A brief general discussion.

L. E. GILSON

Influence of fat and carbohydrate on the nitrogen distribution of the urine. E. P. CATHCART. *Biochem. J.* 16, 747-53(1922).—The fat used was olive oil emulsified with a small quantity of K_2CO_3 . The sugar was dextrose. The expts. were performed on a lab. worker. Each expt. lasted 3 days, and the successive diets were as follows: 323 g. olive oil; 323 g. olive oil; 310 g. olive oil and 30 g. dextrose; 297 g. olive oil and 60 g. dextrose; 279 g. olive oil and 100 g. dextrose; 257 g. olive oil and 150 g. dextrose. The calorific values varied between 3102 with pure oil and 2978 with oil + 150 g. sugar. The subject "found it impossible to carry on for more than 3 days on account of the nausea induced by the mere sight and smell of the emulsified oil." The output of total N, urea and NH_3 rises on a fat diet and falls on the addns. of carbohydrate. The reverse is true of uric acid. Creatinine is but little affected. Small amts. of creatine are excreted on a carbohydrate-free diet. (See also C. A. 5, 549)

B. H.

Food value of mangolds and the effect of deficiency of vitamin A on guinea pigs. ELLEN BOOCK AND JOHN TREVAN. *Biochem. J.* 16, 780-791(1922).—An epidemic outbreak occurred among guinea pigs fed on mangold, bran and oats and water. The deficiencies in such a diet consist of vitamin A, Ca salts, and the quantity or compn. of the protein. The development of xerophthalmia in the guinea pig is recorded, as well as its cure with cod-liver oil.

BENJAMIN HARROW

Vitamin D. T. B. HEATON. *Biochem. J.* 16, 800-10(1923).—The expts. recorded support Funk's view of the existence of a 4th vitamin (vitamin D), which is held to be the "yeast-activating substance," and which is considered identical with Wildiers "bios." "The deprivation of water-sol. vitamin from rats is held to involve a double deficiency; a deficiency of vitamin B in the first place, and of the yeast-activating substance in the second." It seems evident that vitamin B is to be regarded as that vitamin which cures birds of polyneuritis.

BENJAMIN HARROW

Mammary secretion. IV. The relation of protein to other dietary constituents. G. A. HARTWELL. *Biochem. J.* 16, 825-37(1922); cf. C. A. 16, 2169.—Mother rats were fed on an excess protein diet, to which were added various fruits and vegetable juices and exts. made from other foods said to contain vitamin B. It appears that the addn. to the mother's protein-rich diet of juices of, or exts. from, foods reported to contain vitamin B, is effective in rendering the nature of the milk more normal.

BENJAMIN HARROW

Report of the Director of Veterinary Education and Research. ARNOLD THEILER. *J. Dept. Agr. Union S. Africa* 5, 527-34(1922).—P is the limiting factor in the growth rate of cattle and a dominant factor in the maintenance of live-wt. under ordinary conditions of grazing. In horses, mode of life and activity influences the number of red corpuscles in the blood, rather than sex, food or water.

K. D. JACOB

Relation between state of nutrition and complement titer in guinea pigs. HILGERS.

Centr. Bakt. Parasitenk., I Abt. 89, 217-19(1922).—In undernourishment the complement titer in guinea pigs is reduced.

JULIAN H. LEWIS

Respiratory exchange and basal metabolism during a fast of forty-three days duration. MARCHÉ LABBÉ AND HENRI STÉVENIN. *Compt. rend. soc. biol.* 87, 607-10 (1922).—The subject of this prolonged fasting expt. was a man 42 yrs. of age, weighing 62.7 kg. and having a body surface of 1.7 sq. m. The metabolism expts. were made by the Tissot method, the person resting on a couch during the test. The CO₂ production before the fast was 3.1 cc. per kg. and per min. It gradually diminished in the course of the fast and was only 1.7 cc. on the last fast day when the body wt. decreased 25%. The O consumption at first increased but after the 5th day it also began to diminish and on the last fast day it was only 2.5 cc. per kg. and per min. The respiratory quotients found are almost invariably below 0.7. These low respiratory quotients are thought to be due to the formation of acetone bodies because the lowest values correspond to the period of the highest elimination of these bodies, and the diminution in their excretion also coincides with a rise in the quotients. The basal metabolism at first rises from the normal of 39.5 Cal. per sq. m. to 46.2 Cal. on the 5th fast day and then gradually declines to 21.7 Cal. on the last day. The realimentation period is also marked by a lower basal metabolism though the subject's wt. is restored to normal in 29 days. No data are given as to the diet after the fast.

S. MORGULIS

Practical discussion of army rations as they are and as they should be. M. BARTHÉLÉMY. *Rev. soc. hyg. aliment.* 10, 487-510(1922).

A. P.-C.

The effect of cooking upon the vitamin content of cabbage (Eddy, *et al.*) 12.

BERG, REGNAR. *Die Vitamine*. Leipzig: S. Hirzel. 336 pp. Reviewed in *J. Am. Med. Assoc.* 79, 2107(1922).

PIRQUET, CLEMENS. *An Outline of the Pirquet System of Nutrition*. Philadelphia and London: W. B. Saunders Co. 96 pp. \$2. Reviewed in *Am. Food J.* 18, 24 (1923).

F—PHYSIOLOGY

ANDREW HUNTER

Action of ingested chlorides on gastric secretion. A. FROUIN. *Bull. soc. chim. biol.* 4, 435-53(1922).—Expts. on dogs with the stomach either completely isolated (cardiac and pyloric ends joined) or with a small isolated stomach (Haidenhain-Pawlow-Chighin procedure) show that there is a min. of NaCl (or other chloride) necessary to provoke gastric secretion, maintain appetite and nutrition, which for dogs is between 2 and 3 g. per day. The amt. of gastric secretion and acidity are proportional to the chloride in the diet. Peritoneal or intravenous injection of chloride produces the same effect as feeding by mouth in restoring normal conditions in such animals emaciated through chloride starvation. There is therefore an action of NaCl on intestinal digestion and general metabolism.

A. T. CAMERON

The relation of colloidal chemistry to physiology. EMIL ABDERHALDEN. *Kolloid-Z.* 31, 276-9(1922).—A review. The cell must be considered as a colloidal system. The old idea of a cell wall is being replaced by the conception of a cell border consisting of colloidal particles. Fertilization is discussed; it is believed that its exact nature will be cleared up through a better knowledge of the colloids. Muscle contraction and relaxation, mental processes and nerve impulses must be considered colloidal in nature.

A. A. CHRISTMAN

The physiological transformation of protein compounds. ALBRECHT KOSSEL. *Naturwissenschaften* 10, 999-1005(1922).—A review and discussion. C. C. DAVIS

The effect of partial and total extirpation of the thyroid and parathyroid glands upon blood enzymes. MAGATH. *Z. ges. expil. Med.* 29, 264-72(1922).—The thyroid gland regulates protein metabolism in the sense that its secretion acts as a kinase for those enzymes which are concerned in the synthesis and analysis of proteins. The parathyroids regulate sugar metabolism in the sense that they furnish a kinase for amylolytic enzymes. The thyroid secretion acts as a kinase for the catalase of the cell elements.

E. B. FINK

The distribution of metabolites in the blood and tissues. HAROLD RYPINS. *Arch. Internal Med.* 30, 578-92(1922).—In cases in which the blood metabolite level was not increased above normal, the concn. of sugar in serous effusions averaged 83.4%, that of urea 80.1% and that of creatinine 67.3% of the amts. found in the blood. In the spinal fluid, these values were 44.2%, 58.2% and 68.3%, resp., except in cases of acute meningitis, in which no sugar was found in the spinal fluids. In cases in which the blood metabolite level was raised, the concn. in the body fluids was increased so that the ratio of concn. in fluid to concn. in blood was higher than normal. No characteristic difference in metabolite concn. of exudates and transudates was observed. I. G.

The intestinal digestion of connective tissue. J. BUCKSTEIN. *Arch. Internal Med.* 30, 761-6(1922).—A metal tip was sewed to an intestinal tube by means of kangaroo tendon. By means of the X-ray, the tip was observed to become sepd. from the tube in 1 or 2 days after its introduction into the intestine. This occurred even in a patient with achylia gastrica, with proven absence of gastric enzymes, whose gastric contents did not digest the tendon in 30 days. Connective tissue digestion is not dependent upon the secretion of active gastric juice. I. GREENWALD

The carbon dioxide and oxygen content of stomach gas in normal persons. A. D. DUNN AND WARREN THOMPSON. *Arch. Internal Med.* 31, 1-8(1923).—"Atmospheric air introduced into the stomach tends to come into equil. with the blood (and tissue) gases within 1 hr. in the case of CO₂ and considerably later, if at all, in the case of O₂." A CO₂ content up to 9% may be found in normal individuals. I. G.

The effect of olive oil on gastric function as measured by fractional analysis. B. C. LOCKWOOD AND H. G. CHAMBERLIN. *Arch. Internal Med.* 31, 96-101(1923).—"The administration of 1 oz. of olive oil before meals causes a reduction of the av. acidity and a lowering of the high point of acidity by about 12% (cc. 0.1 N acid per 100 cc. contents). It also causes a delayed evacuation for the bread of an Ewald meal for 40 min. longer than in the control and the oil remains at least 15 min. longer. It also causes a regurgitation of bile in about 80% of the cases. I. GREENWALD

The relations existing between arterial and venous blood of the dog with special reference to the plasma chlorides. E. A. DOISY AND J. W. BECKMANN. *J. Biol. Chem.* 54, 683-91(1922).—In 22 expts. upon dogs blood was drawn from arteries and veins exposed under cocaine or butyn anesthesia. Analyses of the blood and plasma indicated that, in the change from arterial to venous blood, the vol. of the cells increased by an av. of 0.35%, the NaCl content of the plasma diminished by an av. of 0.00138 M, the CO₂ content of the plasma increased by an av. of 0.00196 M, the ratio of increase in CO₂ to decrease in O₂ was from 0.58 to 1.05, and, of the increase in CO₂, 37.5-75.7, av. 52.4%, was carried by the corpuscles. The discrepancy between loss of plasma Cl and increase of plasma CO₂ may be due to physically dissolved CO₂, to the "self-possessed" buffer action of the plasma and the increased vol. of the cells, which was not considered in these calcs. I. GREENWALD

Colorimetric studies of tryptophan. VII. The tryptophan requirements of growing rats together with a contribution to the problem of cyclopoiesis. O. FÜRTH AND F. LIEBEN. *Biochem. Z.* 132, 325-42(1922); cf. *C. A.* 16, 275.—An extensive study based on 8 albino rats. The animals were fed exact amts. of food of known tryptophan con-

tent for 22 to 25 weeks and the amts. fed compared with the total tryptophan contents of the rats at the end of the period of study. From 3 to 8% of the tryptophan of the diet was incorporated into the rats, by far the greater portion being destroyed. The results are therefore in agreement with the cyclopoietic hypothesis of the inability of the organism to synthesize the cyclic complexes. The min. tryptophan requirement of the growing rat from any protein source (*e. g.*, yeast, milk or meat) is 0.07–0.13 g. per kg. per day. This value exceeds that of human nurslings by 100% and is from 3 to 6 times that of growing (adolescent) youngsters. This greater requirement of the rat is attributed to the relatively greater gas exchange and body surface. A luxus consumption of tryptophan does not seem to accelerate the growth of rats or increase the body tissue content of the compd. The rat body contains about 0.22% tryptophan, a value similar to the mean tryptophan content of the human body. F. S. HAMMETT

Vagus and sympathetic function. The identity of nerve and ion action. S. G. ZONDEK. *Biochem. Z.* 132, 362–92(1922).—From the point of view that the function of the organs depends just as much on the balancing of the vegetative nerves as on the balancing of certain inorg. cations, the question of a relation between nerve and action activity was studied. Na and K effect simulated vagus action and the Ca effect is like that of the sympathetic. Where the vagus causes stimulation (intestine, bladder) Na and K act likewise; where vagus stimulation is inhibitory (heart), so do Na and K act as inhibitors. The same holds true for the sympathetic. Not only do nerve and ion action run parallel but they are interchangeable. From these exptl. findings an hypothesis is built up of the inter-relationship between ion and nerve action, in which disturbances of equil. in the one system induce disturbances in equil. of the other.

F. S. HAMMETT

Excretion of cholesterol in the urine. W. GRUNKE. *Biochem. Z.* 132, 543–55 (1922).—The method of Autenrieth and Funk (*C. A.* 7, 2953) as modified by Weston was used for the detn. of the urinary cholesterol, with the additional procedure of using $\text{Ca}(\text{OH})_2$ as a clarifying agent instead of Na_2SO_4 and dissolving $\text{Ca}(\text{OH})_2$ residue in HCl and extg. with CHCl_3 to obtain any cholesterol that might be adsorbed. $\text{Ca}(\text{OH})_2$ removed the bile pigment derivs. of sapon. from the CHCl_3 ext. Only traces of cholesterol are found in normal urine (1.0 mg.). Out of 9 cases of icterus, one showed 10.1 mg. per day, with 0.182% in the blood serum. Of 5 urines from diabetics, one contained 12.9 mg. per day with 0.236% in the serum. Hence the blood cholesterol cannot be considered a definitive index of cholesterol excretion. On the other hand the harmful effect on the kidneys presumably caused by cholesteroloria was not a significant causative factor in the cholesterol excretion observed here, since no renal lesions could be detected clinically. The urinary sediment was too slight to account for the cholesterol found.

F. S. HAMMETT

Blood reaction and blood corpuscle volume. K. MEIER. *Biochem. Z.* 133, 67–74 (1922).—Just as there occurs an irregularity in the CO_2 -binding curve of the blood with changing reaction so there occurs a similar irregularity in the curve of blood-corpuscle vol. and at the same reaction. While the vol. of the erythrocytes increases at first regularly with increasing CO_2 tension and H-ion concn. the increase becomes irregular at a certain reaction.

F. S. HAMMETT

The influence of cooling on the creatine of muscles. A. PALLADIN AND A. KUDR-JAWZEEFF. *Biochem. Z.* 133, 89–96(1922).—When rabbits are cooled so that the body temp. falls the creatine content of the musculature increases. The creatine content reaches its max. 12 hrs. after the cooling and then gradually returns to normal by the end of the 2nd day. Since the tonic activity of the muscles is increased by the lowering of the body temp. it would appear that there is a relation between muscle tonus and creatine formation. The fact that the increased muscle creatine on cooling is accompanied

with an increased creatine excretion in the urine tends to support the idea of the origin of urinary creatine and creatinine from the creatine of the muscles. F. S. HAMMETT

The influence of sugar puncture on the alkali reserve of the blood of rabbits. F. KORNFIELD AND U. SAMMARTINO. *Biochem. Z.* 133, 212-4(1922).—A tendency to decreased hydron concn. of the blood occurs after puncture in rabbits. The alkali reserve rose in some animals and fell in others. In general, however, the alkali reserve and the CO_2 content of the arterial blood tended to be somewhat lower in the test animals. The possibility of participation in the reaction of the operative trauma is noted.

F. S. HAMMETT

Lactic acid formation after sugar puncture. V. SAMMARTINO. *Biochem. Z.* 133, 215-7(1922).—Puncture of rabbits is followed by an increase in the lactic acid content of the liver, but not to as great an extent as follows adrenaline administration.

F. S. HAMMETT

Relation between the sugar content of blood plasma and cerebrospinal fluid. ST. RUSZNYÁK AND L. CSÁKI. *Biochem. Z.* 133, 355-7(1922).—A series of detns. of the reducing sugar content of blood plasma and cerebrospinal fluid taken from the same individual at the same time. In non-diabetic persons the sugar content of the cerebrospinal fluid is always less than that of the blood plasma and is about 0.05%. In diabetics, notwithstanding the high sugar content of the cerebrospinal fluid, the same relative condition obtains as in non-diabetics. However, it is possible that when sudden changes in blood sugar occur, because of the sluggish change in cerebrospinal fluid, higher values may be found in the latter than in the former.

F. S. HAMMETT

Physicochemical studies on body fluids. V. Remarks on the question of the state of the chlorine and sugar in serum. ST. RUSZNYÁK. *Biochem. Z.* 133, 358(1922).—Polemical. VI. The reduced viscosity of serum. *Ibid* 359-64.—The viscosity of freshly drawn blood from various individuals was detd. after preliminary concn. by ultrafiltration to 10%. In sera from normal persons this "reduced" viscosity averaged 2.35, while in edema and hydremic renal disturbances a significant increase obtained.

F. S. HAMMETT

Glandular physiology. LIV. L. ASHER. Demonstration of adrenaline in arterial blood. C. SCHNEIDER. *Biochem. Z.* 133, 373-90(1922); cf. *C. A.* 16, 1980.—Rabbits were used in these expts. The superior cervical ganglion of one side was extirpated. The injection of strychnine into the otherwise uninjured animal produced a marked pupillary dilation on the side of the operation and only a minor similar reaction on the normal side. After the splanchnic nerves had been extirpated on both sides the pupillary reaction to strychnine could not be produced. The latter phenomenon is attributed to a lack of increased adrenaline secretion following the strychnine stimulation of the splanchnics, and is a proof of the presence of adrenaline in the major circulation under normal conditions.

F. S. HAMMETT

Studies of cell permeability. X. The influence of the nerves to the blood vessels on vascular permeability, particularly those of the anterior chamber of the eye. J. KAJIKAWA. *Biochem. Z.* 133, 391-404(1922).—Ca inhibition of inflammation by mustard oil was established. When the superior cervical ganglion is extirpated the inflammatory action of mustard oil on the operated side was diminished and the action of Ca thereon less marked. When fluorescein was injected into the peritoneal cavity, its appearance in the anterior chamber of the eye of the operated side was later than its appearance on the unoperated side. The protein content of the liquor on the operated side was less than that of the intact side. All these facts are taken to demonstrate that vascular permeability is decreased when sympathetic innervation is lacking and hence that such innervation exerts an influence on permeability and on the trophic cell activities.

F. S. HAMMETT

Chemistry of the lungs. III. The nucleic acid of the lungs. U. SAMMARTINO. *Biochem. Z.* 133, 406-8(1922); cf. *C. A.* 17, 291.—S. isolated nucleic acid from lung tissue using Levene's method (*C. A.* 15, 4013). The product gave no orcinol reaction. Analysis showed: C 38.1, H 5.2, N 14.2, and P 5.9%, in close agreement with the calcd. formula $C_{24}H_{24}N_{10}P_2O_{24}$. Adenine and guanine picrates were obtained on hydrolysis. Removal of the P by Ba hydrolysis and benzylation according to Schotten-Baumann gave a sirupy ether-sol. product which gave no carbohydrate reaction. S. considers that this nucleic acid is different from that obtained by Levene from other tissues. The lungs are poor in nucleic acid.

F. S. HAMMETT

Influence of the parenteral administration of protein on gaseous metabolism. A. LEIMDÖRFER. *Biochem. Z.* 133, 409-16(1922).—Parenterally administered protein produces an increase in the oxidative processes which is accompanied by a rise in temp. If the latter does not occur there is no change in gaseous metabolism. A discussion of the role of the thyroid in chem. heat regulation is given.

F. S. HAMMETT

The alkali content of blood and cerebrospinal fluid, together with a new method for the determination of sodium. M. RICHTER-QUITTNER. *Biochem. Z.* 133, 417-31 (1922).—The usual ashing methods are unsuitable as preliminaries in the detn. of Na of blood. Ultra-filtration of plasma or serum is to be preferred since practically all of the blood Na is in the free condition. Na in colloidal union could not be detected in blood. The Na was detd. in the ultra-filtrate as $Na_2H_2Sb_2O_7$ after getting rid of the Fe and Ca as usual. A part of the blood K is present in colloidal combination. The loss of CO_2 from the blood has no influence on the Na content of the blood corpuscles. Venous stasis causes shrinkage of the erythrocytes in which escape of salts as well as H_2O occurs. The K content is particularly affected while the Na is not influenced. Hence for K detn. the ash and H_2O content of the blood obtained without stasis must be used. No significant amts. of Na enter the blood corpuscles in pathol. conditions. The Na content of cerebrospinal fluid is generally just the same as is that of plasma or serum, while the K content is significantly less.

F. S. HAMMETT

Physiology and pharmacology of purine metabolism. V. Allantoin excretion by rabbits under various conditions and the influence of poisons. M. YANAGAWA and E. STRANSKY. *Biochem. Z.* 133, 434-45(1922).—Since the allantoin content of urine decreases on standing, detns. should be made within 24 hrs. of collection. In 100 g. of sifted oats there was found 0.01848 g. purine N, 0.06212 g. Ca and 0.1065 g. Mg. In 100 g. fresh carrots there was found 0.00178 g. purine N, 0.0643 g. Ca and 0.1081 g. Mg. Allantoin, uric acid, asparagine and urea were not detected. More allantoin was excreted when the rabbits were fed the oats diet than when fed with carrots. The differences are not attributed to the differences in purine content of the 2 foods but to Ca intake. When rabbits are fasted the allantoin excretion first drops and later rises again. Cooling of the animals produced an increase in allantoin excretion while hyperthermia induced by injection of tetrahydro- β -naphthylamine had no influence. Adrenaline, uzara, caffeine, cocaine, and papaverine increased allantoin excretion. The most marked effect was obtained after adrenaline. A comparison of the reported action of various other drugs leads to the conclusion that a marked influence on purine metabolism is effected by acting on the sympathetic nervous system. **VI. Effect of Karlsbad mineral waters.** E. STRANSKY. *Ibid* 446-58.—Expts. on rabbits and man showed that Karlsbad water has a double effect on purine metabolism, a stimulation of uric acid excretion in man probably due to washing out of uric acid depots which stops after a few days, and a retarding effect which is attributable to an improvement in the Ca balance. Whether or not this is a renal effect is not known.

F. S. HAMMETT

Keratinization. U. SAMMARTINO. *Biochem. Z.* 133, 476-86(1922).—Natural keratins were extd. with alc., digested with artificial gastric juice, dried, ashed or hy-

droylized. Hair, finger-nails and corns were used. The analyses showed that keratins from different sources differ in their content of cystine, tyrosine, tryptophan and glutamic acid. The amt. of these amino acids is much greater in the keratins than in globulin and albumen. On the other hand the aliphatic monoamino acids are less. The hypothesis is expressed that keratins arise from the sol. proteins through a gradual splitting off from the mol. of the aliphatic monoamino acids. F. S. HAMMERT

The "membrane" of the erythrocytes. L. BERCZELLER. *Biochem. Z.* 133, 509-17 (1922).—Suspension expts. with erythrocytes in paraffin oil, olive oil, cedar oil, oleic acid, and the action of the suspensoids, animal charcoal, sea-sand, sol. starch, arrow-root starch, egg albumin, etc., lead to the conclusion that the erythrocytes are not enveloped in an oil-sol. membrane and hence that all assumptions that the degree of hemolysis is parallel to the oil soly. are unsubstantiated. Moreover, certain substances (proteins) which form a ppt. with oleic acid inhibit hemolysis. The hemolytic action of adsorbents shows the same facile adsorbability of substances which form membranes. The behavior of the erythrocytes towards salt solns. showed that they possess no membrane of const. compn. but that it depends on the properties of the limiting phases. F. S. HAMMERT

Uric acid excretion and destruction in man. H. CHANTRAIN. *Biochem. Z.* 133, 613-25(1922).—The results of these expts. indicate that Na urate is not decompd. in the human body and that the daily variations in uric acid excretion are not dependent on the formation of uric acid but on particular excretory stimulants. F. S. H.

Studies of blood coagulation. V. The thrombin of Alexander Schmidt. B. STUBER AND M. SANO. *Biochem. Z.* 134, 239-49(1922).—An inquiry into the possibility of thrombin activity being enzymic in nature. Completely deproteinized thrombin solns. are incapable of causing coagulation in fibrinogen solns. Min. traces of protein suffice to induce coagulation. Sulfosalicylic acid was used for testing for protein. The coagulation time is directly dependent on the protein content of the thrombin soln. The protein-free dialysate of thrombin solns. does not bring about coagulation; the contents of the dialysing thimble do. The protein content of the fibrinogen soln. is not of significance in coagulation, but its NaCl content is of great importance. The optimum concn. of NaCl is from 1 to 2%; above that the coagulation time is lengthened. When thrombin is sepd. from fibrinogen soln. by a semi-permeable membrane, the latter is coagulated. From these expts. it is concluded that the manner of action of thrombin is a simple swelling process, by which fibrinogen is deprived of its solvent and thereby coagulated. This colloid chem. interpretation destroys the idea of enzyme activity. Schmidt's thrombin is considered as an artificial product, the purely phys. chem. action of which in coagulation is due to its method of prepn. That is to say the thrombin prepd. according to Schmidt is nothing more than an emulsion of denatured serum albumin and globulin. VI. The mode of action of thrombokinase. *Ibid* 250-9.—Fresh, bloodless liver was macerated, transferred to a dark flask with the same vol. of alc. in a CO₂ atm. and shaken for 3 to 4 hrs. During this time the alc. was renewed until the ext. was colorless. The residue was then extd. several times with petrol-ether, the exts. were combined and evapd. to dryness in the dark, either in vacuum or over H₂SO₄. The residue was taken up in NaCl soln. Another method of extn. is described which did not yield as good a product. Expts. are reported which demonstrate to S. & S. that the action of thrombokinase rests primarily upon substances contained in it which have an action on surface tension, and secondarily on an optimal p_H of 6.4 to 7.0. Hence thrombokinase activity is considered as purely physico-chem. and not enzymic in nature. VII. The role of calcium in blood coagulation. *Ibid* 260-8.—Ca is not a necessary factor in the coagulation of blood since Sr may bring about coagulation in a Ca-free plasma. Ca is considered to have only the general significance of the bivalent cations

in the sense of a sensitization resulting in the pptn. of protein material. Its favorable action on coagulation in certain concn. and its inhibitory effect when the optimal concn. is overstepped rest solely on the laws of colloid chemistry. Ca has no sp. action. The incoagulability of oxalate and citrate blood does not depend on the elimination of the Ca but on the formation of a max. ionized and hence incoagulable fibrinogen complex. The reoccurrence of coagulation in such a blood by diln. or the addition of more salts particularly those of the alk. earths is based on the reduction in the ionization of the fibrin complex.

F. S. HAMMETT

The tryptophan and tyrosine content of hemoglobin and other blood proteins. U. KIKUYAKI. *Biochem. Z.* **134**, 322-35(1922).—Globin was prepd. by various methods. It contained an av. of 3.6% tryptophan as detd. by the Voisenet reaction. When the protein concn. in the solns. under investigation falls below a certain limit, not only are too small values obtained by the above method, but also the reaction may be lacking entirely. The insol. melanoidin arising during acid hydrolysis of proteins (carbohydrate complexes excluded) is relatable to tryptophan, since some 3.3% of melanoidin compds. are obtained under such conditions. Hemoglobin gives up its tryptophan during tryptic digestion only with difficulty. The max. amt. produced by a combination of intestinal juice of the dog and a highly active trypsin prepn. during the course of 3 weeks was but 18% of the amt. actually present. The tyrosine content of globin is between 3.5 and 4.0%. The tyrosine and tryptophan contents, resp., of serum albumin are 5.7 and 1.4, of serum globulin 6.6 and 4.0, and of fibrin 5.3 and (5.3)%. Although further studies may give more exact values it is noteworthy that for each mol. of tryptophan, globin and fibrin contain 1 mol. of tyrosine, serum globulin 2 mols. and serum albumin 5 mols.

F. S. HAMMETT

Remarks on the article by J. deHaan: "The glycogen content of the white blood cells." L. HABERLANDT. *Biochem. Z.* **134**, 405-6(1922). Polemical. Cf. C. A. **16**, 1977.

F. S. HAMMETT

Acetaldehyde in the intermediary metabolism of surviving muscle. J. HIRSCH. *Biochem. Z.* **134**, 415-23(1922).—Frog muscle tissue was macerated and tested for MeCHO. The amt. found was not increased when the tissue was suspended in NaCl soln. and aerated. MeCHO was also isolated from the muscle tissue of *Tinea vulgaris* and *Cyprinus carpio*.

F. S. HAMMETT

Influence of the spleen upon red blood corpuscles. I. N. A. BOLT AND P. A. HEERES. *Biochem. J.* **16**, 754-64(1922).—See C. A. **17**, 412.

B. HARROW

Blood of equines. C. P. NISER. *Biochem. J.* **16**, 770-8(1922).—Erythrocyte counts vary from below 6.3 million for permanently stabled horse to 12 million for race-horses in hard training. The leucocyte count varies between 5.6 and 15 thousand for adult horses. The av. size of erythrocytes is 5.5 μ . "By far the most striking observations recorded concern the remarkable influence of regular exercise upon the proportion of erythrocytes in horse blood."

BENJAMIN HARROW

The mechanism of absorption from the intestine. SAMUEL GOLDSCHMIDT. *Physiol. Rev.* **1**, 421-53(1921).—A review. "It must be apparent that the mechanism of intestinal absorption is qualitatively explained by the known laws of osmosis. Other factors than osmosis may be active in modifying the process. All the evidence points to their physico-chem. nature, and much useful research may still be expended before one need seek refuge in that last resort 'vital cell activity.'"

E. R. LONG

The effects of the subcutaneous injection of splenic extract. A. W. DOWNS AND N. B. EDDY. *Am. J. Physiol.* **62**, 242-7(1922).—Protein-free ext. of desiccated spleen injected into rabbits caused: (1) increased destruction of red blood cells, (2) increased production of red blood cells, (3) increased proportion of reticulated cells in the circu-

lating blood, (4) increased resistance of the red cells to hemolysis by hypotonic NaCl solns., (5) the appearance of nucleated red cells in the circulating blood. J. F. L.

Nervous control of the kidney in relation to diuresis and urinary secretion. VI. The effect of unilateral section of the splanchnic nerve on the elimination of certain substances by the kidney. E. K. MARSHALL, JR. AND M. M. CRANE. *Am. J. Physiol.* 62, 330-40(1922).—Increased blood flow through the kidney, brought about by section of the splanchnic nerve, increases markedly the elimination of H_2O , chlorides and carbonates, to a less extent that of urea, phosphates and sulfates, while the elimination of creatinine, NH_4 and phenolsulfonephthalein is unchanged. The results are thought to support the theory of filtration through the glomeruli and reabsorption and secretion by the tubules.

J. F. LYMAN

Studies in fatigue. XII. The effect of adrenal secretion on non-fatigued and fatigued skeletal muscle. C. M. GRUBER. *Am. J. Physiol.* 62, 438-41(1922); cf. C. A. 16, 3513.—Adrenaline secreted by splanchnic stimulation affects non-fatigued and fatigued muscle alike (increases height of muscular contraction and irritability) and hence cannot be regarded as a sp. antagonist to the so-called fatigue substances.

J. F. LYMAN

The output of sugar from the liver as affected by hydrogen-ion concentration and minimal epinephrine. C. D. SNYDER, L. E. MARTIN AND M. LEVIN. *Am. J. Physiol.* 62, 442-58(1922).—Ringer solns., buffered with phosphates, some of which were neutral or slightly acid and others a little more alk. than normal blood, were perfused through terrapin liver and the perfusion rate and % of dextrose in the outflow detd. Acid appears to produce vasodilatation and increased outflow; alkali vasoconstriction and diminished outflow. The output of reducing substances (dextrose) from the liver per min. was greater for the more acid perfusates and lower for the more alk. ones. When minimum effective amts. of adrenaline were added to the perfusing fluids of high and low p_H , (1), the min. vol. outflow for the more alk. solns. was markedly less, and for the more acid solns. markedly greater, than for adrenaline-free solns. of equal acidity; (2), the min. output of dextrose for the alk. solns. was less, and for the more acid solns. greater, than for adrenaline-free solns. of equal p_H . The role of adrenaline in great diln. is not concerned directly so much with mobilization of sugar from the liver as it is with detg. the amt. of fluid flowing through its portal-venous bed. J. F. L.

The influence of adrenaline on metabolism in various excised tissues. E. G. MARTIN AND R. B. ARMISTEAD. *Am. J. Physiol.* 62, 488-95(1922); cf. C. A. 16, 2719.—The addition of adrenaline (concn. 1:200,000) to Ringer soln. in which various excised frog tissues were immersed caused an increase in the rate of acid production (CO_2) as follows: brain 160%, mesonephric tissue 200%, liver 150%, stomach 60%, intestine 33%. The thermogenic influence of adrenaline is not sp. for any one kind of tissue but extends to most sorts, if not to all.

J. F. LYMAN

The effects of insulin on experimental hyperglucemia in rabbits. F. G. BANTING, C. H. BEST, J. B. COLLIP, J. J. R. MACLEOD AND E. C. NOBLE. *Am. J. Physiol.* 62, 559-80(1922).—The rise in blood sugar normally caused in rabbits by puncture, adrenaline, mechanical or CO asphyxia and ether is either prevented or greatly limited by the subcutaneous injection of insulin (purified EtOH ext. of pancreas). Cf. C. A. 16, 3115; 17, 580.

J. F. LYMAN

Partition of urea in the blood. M. POLONOVSKI AND C. AUGUSTE. *Compt. rend. soc. biol.* 87, 681-2(1922).—Invariably less urea (detd. gravimetrically as xanthyl urea) is found in the entire blood than in the plasma. Similar results are obtained in an artificial blood. A correction is proposed for vol. of red cells which is intended to give the real amts. and which is based on the study of the urea distribution in the artificially made up bloods.

S. MORGULIS

Urea equilibrium in the cerebrospinal fluid. M. POLONOVSKI and C. AUGUSTE. *Compt. rend. soc. biol.* 87, 683-4 (1922).—Since there is a certain const. difference between the urea content of venous blood and that of the cerebrospinal fluid the latter may be in equil. with the blood of the choroid plexus, which is more closely related to the arterial than to the venous system. The urea content of the arterial blood is less than that of the venous blood in the dog. S. MORGULIS

Role of adrenaline in hypertension resulting from the stimulation of the splanchnic nerve or from bulbar puncture. B. A. HOUSSAY. *Compt. rend. soc. biol.* 87, 695-8 (1922); cf. *C. A.* 17, 830.—Stimulation of the splanchnic nerve causes a much greater rise in arterial pressure when the suprarenal veins are free than when these are clamped off. Plethysmographic records of the limb show a brief passive dilatation followed by a constriction when the veins are open, which fails to appear when the veins are pinched off. The constriction reappears upon releasing the veins. The action of the adrenaline is, therefore, considered to be vasoconstrictive and is exerted directly on the neurovascular mechanism. In animals properly prep'd. (previous extirpation of the right adrenal body, spinal cord section, vagus section, and artificial respiration) puncture of the medulla causes strong hypertension. When the veins are clamped the limb dilates passively but when the vein is open there follows a strong and prolonged constriction. H. has shown previously that adrenaline is not necessary to maintain life or vascular tone by removing the medullary layer from the left adrenal body after complete removal of the right body without endangering the animal's existence. From the present expts. on splanchnic stimulation or stimulation of the bulbar nerves he concludes that under these conditions enough adrenaline is produced to reveal the physiol. effect without any doubt. S. MORGULIS

Studies in the gastric juice. IV. The pyloric juice. MAKI TAKATA. *J. Biochem. (Japan)* 2, 33-42 (1922); cf. *C. A.* 16, 1614.—The pyloric juice was obtained from a small stomach with nerves intact. The rate of secretion from the pyloric pouch in the dogs was 0.5 to 1 cc. per hr. and little increase could be observed towards the end of gastric digestion. The secretion is thick, viscid, faintly alk. and contains mucin flakes; d_{18} 1.009-1.012. The H-ion concn. measured by the gas-chain method on 15 samples varied between 10^{-3} and 4×10^{-3} . No trace of HCl could be found in this juice. Its av. compn. is H_2O 97.72, ash 0.94, Na 0.24, K 0.06, Ca 0.013, Mg 0.006, Cl 0.53, S 0.004, P 0.02% and Fe trace. An enzyme of peptic character is present in the juice, as this will digest fibrin and egg-white in the presence of HCl (2-3 per 1000 is the optimum concn.), though the juice neither as it is secreted nor when mixed with varying amts. of Na_2CO_3 had been found active. The pyloric juice of the dogs used is capable of effecting weak but distinct clotting of milk, indicating the presence of rennin. A lipase is present, which can act upon fats but hardly attacks pure lecithin. There is a small though detectable amt. of nuclease. Trypsin if present at all must be in mere traces only as its action could not be demonstrated. There can be no doubt as to the presence of an amylase. For sucrase the expts. are negative. The enzymatic compn. of the pyloric juice from the dog is similar to that of the empty stomach juice, though quant. these 2 vary. Thus, for instance, pepsin and lipase are much more conc'd. in the gastric juice while amylase in the latter is for all practical purposes absent. S. MORGULIS

The glucolytic activity of blood. YOSHIKANE KAWASHIMA. *J. Biochem. (Japan)* 2, 131-71 (1922).—The serum and the plasma of the blood have no glucolytic action. The glucolytic power of the red cells from healthy rabbits does not depend upon the sugar concn. within the limits of 0.155 to 0.317%, but is chiefly dependent on the number of red cells. The glucolytic activity is directly proportional to the number of erythrocytes for the same sample of blood. The glucolytic activity of the erythrocytes in

serum or in a phosphate mixt. of the same alkyl. as blood is greater than in physiol. salt soln. It is the same in the latter as in Ringer soln. Hemolysis brought about by various phys. or chem. means diminishes the glucolytic power according to the degree of hemolysis produced. When the hemolysis is complete the glucolytic capacity is also entirely gone. CN and toluene are without effect on glucolysis of the blood provided they are not present in sufficient concn. to cause hemolysis. Alc., Et_2O , CHCl_3 , quinine-HCl and hypotonic salt soln. act similarly. Red cells treated with abs. alc. have no glucolytic action. The absence of O_2 does not alter the glucolytic activity of the blood, neither does excessive oxygenation. CO behaves in a similar manner. CO_2 in large amt. interferes with the glucolytic action of the blood but this is again restored when O_2 is passed through it. It seems that glucolysis is entirely due to erythrocytes while the leucocytes which are always attached to them in minute amts. are apparently without appreciable glucolytic action. In the ice box the erythrocytes retain their glucolytic power for a very long time; at 37° they lose their function and also their glucolytic activity in 24 hrs. The glucolytic capacity of the erythrocytes might be utilized as a measure of the vitality of the cells.

S. MORGULIS

Effect of suspended respiration on the composition of alveolar air. H. S. HALCRO WARDLAW. *Proc. Linnean Soc. N. S. Wales* **47**, 545-50(1922).—Previous work has been repeated by different methods, the essential difference being that in the present case the individual periods of holding the breath are so short that disturbances of the circulation are reduced to a min. When the circulatory disturbances are minimized, an approx. const. compn. of alveolar air is reached by holding the breath. This compn. is almost the same whether the breath is held under normal atm. pressure or under a negative pressure of about 30 mm. of Hg. The existence of the const. tension of alveolar CO_2 is confirmed. The higher values for CO_2 and the lower values for O_2 obtained under conditions of negative pressure in the former paper are not due to the direct effect of negative pressure on the compn., but to the acceleration of the circulation, leading to a more rapid accumulation of CO_2 and a more rapid removal of O_2 . A. P.-C.

Influence of glands with internal secretions on the respiratory exchange. VI. Further data on the effect of suprarenal insufficiency (by removal) in rabbits. DAVID MARINE AND E. J. BAUMANN. *J. Metabolic Research* **2**, 1-18(1922); cf. *C. A.* **15**, 3519; **17**, 135.—A prolonged abs. rise in heat production has been obtained in 82% of 33 rabbits in which both suprarenal glands were completely removed, and in 40% of 15 rabbits where the suprarenal function was crippled by freezing. The period of increased heat production may last from a few days to several months; the longest period in which increased thermogenesis has been followed in an individual rabbit was 23 weeks. The increased thermogenesis is in part dependent on the increased rate of discharge of the I-contg. hormone from the thyroid. The ability of the thyroid to store I or to produce this hormone is not impaired after suprarenal injury. Infection, trauma, nerve injury, muscular movement and diet are not essential factors in the increased thermogenesis following suprarenal injury.

W. A. PERLZWEIG

Muscle hardening. I. Method for estimating hardness. ERNST MANGOLD. *Arch. ges. Physiol. (Pflüger's)* **196**, 200-14(1922).—The method is based upon the principle of static sclerometry. **II. Hardness measurements in rigor mortis and in heat rigor.** *Ibid* 215-28.—When tested by this method, dog muscle shows that hardness begins to manifest itself in about 3 hrs. after death, reaching a max. at 24 hrs. post mortem. Increase in muscle hardness is a const. feature of rigor mortis, and differs from muscle shortening. Expts. upon heat rigor show that the two processes, hardening and shortening, are distinct and completely independent of each other. The shortening of dog muscle in heat rigor takes place in two phases at diff. temps.; the hardening process takes place during the first phase of the shortening.

G. H. SMITH

Biological significance of organs of internal secretion. I. Thyroid gland and metamorphosis. C. HART. *Arch. ges. Physiol. (Pflüger's)* 196, 127-50(1922).—External environmental factors operate upon the inception and the course of metamorphosis only through their influence upon the function of the thyroid. **II. Influence of abnormal external temperature on the thyroid and testes.** *Ibid* 151-76.—The degenerative changes observed in the tissues of the thyroid and testes following maintenance of the animals at high temps. are simply an expression of deranged function of the endocrine organs. G. H. SMITH

Blood destruction during exercise. II. Demonstration of blood destruction in animals exercised after prolonged confinement. G. O. BROWN. *J. Exptl. Med.* 37, 113-30(1923); cf. *C. A.* 17, 135.—A great decrease in total circulating hemoglobin and red cell vol. occurs in dogs long maintained under sedentary conditions when they are exercised vigorously during several consecutive days. This would appear to be consequent on increased blood destruction, unrepaired for the time. C. J. WEST

F—PHYSIOLOGY

ANDREW HUNTER

Thermoelectric studies of temperature variations in animal tissues. I. General considerations: description of apparatus and technic. G. W. CRILE, H. R. HOSMER AND A. F. ROWLAND. *Am. J. Physiol.* 62, 341-8(1922).—Thermoelec. couples for detg. temp. of body tissues are described and their use is discussed. **II. Effects of anesthesia, electrical stimulation, abdominal trauma, exposure of viscera, excision of organs, acid, alkali, strychnine, diphtheria antitoxin.** G. W. CRILE AND A. F. ROWLAND. *Ibid* 349-69.—The temp. of brain and liver was measured after these various treatments. **III. Adrenaline.** *Ibid* 370-82.—The temp. of the brain and of the thyroid were increased; the temp. of the liver and of the skeletal muscle were not changed by adrenaline. After removal of the liver, adrenaline produced no effect or a fall in the brain temp. After thyroidectomy the reaction of the brain to adrenaline was diminished. CHI_3 and Et_2O increased the reaction of the brain to adrenaline, while N_2O diminished it. J. F. LYMAN

The utilization of oxygen in the blood at different stages of anoxemia. C. H. GREENE AND C. W. GREENE. *Am. J. Physiol.* 62, 542-56(1922); cf. *C. A.* 16, 2359.—Analyses were made of venous blood, arterial blood and alveolar air in samples taken simultaneously. In the normal animal and in the early stages of anoxemia the arterial blood contains a large excess of O_2 over the requirements of the animal. The O_2 consumption in the tissues is nearly uniform until the venous O_2 reserve is exhausted. Thereafter the O_2 utilization parallels the satn. of the arterial blood. In the dog, respiratory and circulatory crises approach when the alveolar O_2 tension is reduced to from 25 to 35 mm. partial O_2 pressure, or when the arterial blood is between 25 and 35% satd. At these levels the jugular blood returns practically deoxygenated. Below these levels the respiratory and circulatory centers are unable to maintain their normal level of activity. The venous O_2 content represents an O_2 reserve available, apart from the circulatory compensations, for an increased O_2 consumption above the basal level. J. F. LYMAN

G—PATHOLOGY

H. GIDEON WELLS

The prevention and control of parathyroid tetany. A. B. LUCKHARDT AND P. J. ROSENBLUM. *Proc. Soc. Exptl. Biol. Med.* 19, 129(1921); cf. *C. A.* 16, 3698.—Tetany was prevented for 14-51 days in thyroparathyroidectomized dogs by inducing diuresis through the injection of either ordinary or Ca-free Ringer soln. Tetany could

be induced by stopping the injections. It appears that an active diuresis, however produced, with the elimination of toxic compds., prevents tetany. C. V. B

Causes of dyspnea and death in the pneumothorax. DAUTREBANDE AND P. SPEHL. *Bull. acad. roy. méd. Belg.* [5] 2, 533-52(1922).—The dyspnea observed in surgical pneumothorax is due to lack of O in the blood (anoxemia); it can be prevented by administering O₂. R. BRUTNER

Contribution to the study of the intracellular medium in the living cell. The action of certain chemical substances on the cancerous cell. GUSTAVE ROUSSY AND MAURICE WOLF. *Arch. néerland. physiol.* 7, 562-70(1922).—Parts of an epithelioma from the lacteal gland of a mouse are kept for 12 or 18 hrs. in 0.7% KCl soln. or in 0.8% CaCl₂ soln. The macroscopic and the microscopic changes of the tissues due to this treatment are observed. In KCl soln. the tissue becomes soft and the vol. of the cells increases; in CaCl₂ soln. it looks pale, seems to be contracted and the vol. of the cells has decreased. Lactic acid as well as its NH₄ and Na salts are found to act similarly to KCl while the Ca, Mg, Zn and Fe salts of the lactic acid act like CaCl₂. R. BRUTNER

Analysis of sixty cases of gastric anacidity associated mainly with chronic diarrhea and pernicious anemia. C. HUNTER. *Can. Med. Assoc. J.* 13, 38-43(1923).—In most of the 29 cases associated with diarrhea administration of dil. HCl was almost sp.

A. T. CAMERON

Proportions of sulfur in the skin of one-year infants. E. LABORDE. *Bull. soc. chim. biol.* 4, 584-6(1922).—Examn. of tissues of a child of 2.5 months killed by administration of H₂SO₄ showed no free acid. Healthy skin contained 0.152% S, skin burnt with acid 0.373%. Skin of a 4 months child (dead from a violent blow) contained 0.202%; that from a 6 months child (cause of death undetd.), 0.220%; that from a 5 months child (general enfeeblement), 0.198%.

A. T. CAMERON

The diazo reaction, with special reference to urine in measles. G. HUNTER. *Brit. Med. J.* 1922, II, 751-2.—In measles the output of histidine is increased. This histidine then accounts for 85% of the color developed by the diazo reagent.

A. T. CAMERON

Bence-Jones protein in Hodgkin's disease. J. GALLOWAY. *Brit. Med. J.* 1922, II, 1201-4.—Description of a case is included with const. excretion of a protein similar to Bence-Jones' compd., but differing in the following particulars: no coagulation below 75°; full coagulation at 79-82°; only coagulates in presence of a considerable amt. of acid, and salts like NaCl or (NH₄)₂SO₄; not pptd. by HCl under any conditions.

A. T. CAMERON

Importance of the investigation of hepatic function during severe typhoid fever. F. MALMÉJAC. *Bull. soc. chim. biol.* 4, 426-8(1922).—Pigments and bile acids may appear at the height of temp. increase, and disappear 7 or 8 days later. Traces of albumin appear only for 3 or 4 days. Indoxyl persists, with traces of urobilin, longer than bile pigments. Appearance of the bile elements can be considered as sign of severity, and precursor of possible complications, and these should consequently be watched for.

A. T. CAMERON

Chemical composition of dermoid cysts. G. PATEIN. *Bull. soc. chim. biol.* 4, 652-4(1922).—A mediastinal dermoid cyst (from a woman aged 34) contained about 550 g. of sebaceous substance mixed with numerous stiff and discolored hairs. Histological examn. showed a fibrous coat with multiple calcifications, and at one point a budding towards the interior, contg. sebaceous glands, a cartilaginous mass, and especially abundant neo-formation of glandular type. Chem. examn. of the sebaceous mass showed 10.40% ether-sol., 1.90% ash, 10.50% non-fatty org. material, 77.20% H₂O. The ether-sol. part consisted almost entirely of neutral fats. The other org. material

consisted of serine, globulin, and 0.93% of a protein pptd. by AcOH. Bile pigments, cholesterol, and lecithin were absent. A trace of Fe was present. The mass did not decompose on standing in contact with air. Also in *J. pharm. chim.* 26, 369-72(1922).

A. T. CAMERON

Bone suppuration the basic cause of renal calculus in twenty cases following war-wounds. H. E. PAUL. *Can. Med. Assoc. J.* 12, 638-43(1922).—Results indicated in title.

A. T. CAMERON

Gall-bladder problems. W. BOYD. *Can. Med. Assoc. J.* 12, 689-93(1922).—Histochem. examn. showed that diseased gall bladders probably contain deposits of cholesterol esters, while the lipid material in the normal gall bladder of the dog appears to consist of glycerol esters. Moleschott's test for cholesterol (application of H_2SO_4 dild. with 25% H_2O) can be applied directly to tissues. With diseased gall-bladder tissue it gives a henna color, exactly matched by that given with cholesterol oleate, and by adrenal cortex. Quant. estn. (Bloor method) showed strawberry gall bladders to contain 34-60% cholesterol. Some evidence is adduced that in pathol. conditions cholesterol is absorbed from bile by the bladder.

A. T. CAMERON

Colloidal chemistry and immunity. H. DOLD. *Kolloid-Z.* 31, 290-2(1922).—A review. The Ehrlich side chain theory of immunity is discussed and contrasted with the newer theories of immunity, which consider the body as a colloidal system and consider antibodies to be colloidal particles, and immunity reactions as colloidal reactions.

A. A. CHRISTMAN

In memory of Karl Ludwig. J. VON KRIES. *Naturwissenschaften* 11, 1-4(1923).—A centennial address.

C. C. DAVIS

The present status of experimental rickets. NINA SIMONDS. *J. Home Econ.* 14, 601-11(1922).

L. D. ELLIOTT

The ability of normal and inflamed tissue to hold water. E. HAUBERRISSE. *Z. ges. expl. Med.* 29, 200-7(1922).—Mucous membranes the seat of inflammatory changes show a diminished ability to swell when placed in Ringer soln. as compared with normal tissues. It is possible that there is a physico-chem. change in the colloids during inflammation which diminishes their ability to swell.

E. B. FINK

The inhibition of sodium oleate hemolysis by serum in malignant tumors. HERBERT KAHN AND PAUL POTTHOFF. *Z. ges. expl. Med.* 29, 169-89(1922).—Serum inhibits the hemolytic action of spleen, thymus and pancreatic exts. The serum of individuals with malignant tumors shows less inhibitory activity than that of other non-febrile diseases. The same is true of Na oleate hemolysis. On the basis of these observations a method is described for the titration of the degree of inhibition of Na oleate hemolysis as an aid to the differential diagnosis of malignant tumors.

E. B. FINK

Vitamin B and avian beriberi. W. H. DE WYSS. *Lancet* 1922, I, 100-1.—The reduced oxidative power of the tissues in beriberi animals and the production of symptoms of the disease by injection of a substance which inhibits oxidative processes amounts to a proof that the nature of vitamin B deficiency consists in an inhibition of the oxidative power.

E. B. FINK

The relation between complement and cholesterol content of serum. HARRY KORNGSFEELD. *Z. ges. expl. Med.* 29, 190-6(1922).—An increase of cholesterol in the blood is associated with a decrease of complement in the blood.

E. B. FINK

Phlorhizin glucosuria. III. RICHARD WAGNER. *Z. ges. expl. Med.* 28, 378-83(1922).—The amt. of sugar excreted following injection of phlorhizin is independent of the height of the blood sugar level; it is also independent of the dose of phlorhizin injected. It appears that phlorhizin acts upon the kidney cells and causes them to excrete sugar.

E. B. FINK

The mastic reaction in the blood serum. KARL BAUER AND PAULA EDER. *Z. ges. expl. Med.* **29**, 246-50(1922).—Luetic (Wassermann positive) sera give ppts. and turbidity in the middle of the series. E. B. FINK

Physico chemical changes in the blood following surgical operations and diseases. WILHELM LÖHR AND HANS LÖHR. *Z. ges. expl. Med.* **29**, 139-58(1922).—Following protein injections, sterile operations and diseases associated with a loss of red cells there is an increase of fibrinogen in the blood. Associated with this there is an increase in viscosity of the plasma. The surface tension is decreased, and there is a change in the proteins from the albumin toward the globulin side. The most marked effects follow surgical operations. The results following single injections of foreign protein are not uniform. E. B. FINK

Diseases of the organs of internal secretion and their influence upon blood coagulation. MARGARETE A. BUSSE. *Z. ges. expl. Med.* **28**, 423-48(1922).—There is a decrease in fibrinogen of the blood in hypothyroidism (myxedema), eunuchoidism and dystrophia adiposo genitalis. E. B. FINK

Protective action of the warm chamber upon animals poisoned with protein digestion products. HERMANN PRIFFER. *Z. ges. expl. Med.* **29**, 46-86(1922).—In animals that have been severely burned, or in whom there has been a severe photodynamic action or that have received an intravenous injection of trypsin, there is a disturbance of the temp. regulatory mechanism. Such animals may be saved by placing them in a warm chamber. E. B. FINK

Intravital hemolysis. III. The mechanism of destruction of foreign and toxic homologous blood corpuscles. R. BIEHLING AND D. ISAAC. *Z. ges. expl. Med.* **28**, 154-80(1922); cf. *C. A.* **16**, 435.—Sheep blood corpuscles undergo intravital hemolysis when injected into the blood stream of mice. The mechanism of this type of hemolysis is in many respects similar to that following the injection of immune hemolysin. The sheep corpuscles unite with amboceptor while in the blood stream, but do not undergo hemolysis there. They are destroyed in the splenic pulp and may give rise to acute splenic tumor. The blood pigment resulting from destruction of red cells may be excreted through the kidney as hemoglobin or methemoglobin. Icterus was not observed nor were there any signs of shock or hemorrhages. IV. The function of the reticulo-endothelium. *Ibid* 180-92.—For the production of hemolysin an intact reticuloendothelium is necessary. E. B. FINK

Complement formation in the guinea-pig liver. (Studies on the perfused organ.) O. OLSEN. *Biochem. Z.* **133**, 24-29(1922).—The serum-free guinea-pig liver can disintegrate sensitized blood corpuscles when they are perfused through it. The effect is hastened if amts. of end or middle pieces insufficient of themselves to produce soln. are added to the perfusing mixts. This indicates a lack in certain complement constituents. Apparently this lack is in the direction of the so-called 3rd component. When this component (serum held at 55° for 15 min.) is added to the closed circulating system all the other constituents are formed in large amts. and the sensitized sheep blood corpuscles are quickly dissolved. No detectable amts. of middle or end pieces can be found in the press-juice of the serum-free liver. Hence it is likely that the phenomenon is a matter of the formation of the complement constituents by the liver cells during the course of the perfusion. F. S. HAMMETT

The biochemistry of the pathology following intracarotid centrally directed injections of sheep hemolytic rabbit sera. J. FORSSMAN. *Biochem. Z.* **133**, 114-125 (1922).—By the intracarotid injection into guinea pigs of colored oil emulsions centrally a much larger amt. of the injection fluid reached the medulla oblongata and cerebellum than by peripheral injection. This explains the symptoms arising from similar methods of administration of sheep hemolysins. F. S. HAMMETT

Kidney function in anemia. H. ESSEN AND O. PORGES. *Wiener Arch. inn. Med.* 5, 195-220(1922).—The functioning of the kidney was studied in 10 cases of pernicious anemia and 2 cases of secondary anemia. Volhard water excretion and concn. tests indicated marked renal insufficiency. In severe anemias there was a decrease in the sp. gr. of the urine with only a moderate degree of polyuria. The anemia was accompanied by edema and hydremia, which was not affected by diuretics. With an improvement in the anemia, the sp. gr. of the urine increased and the edema and hydremia decreased. The residual N was not increased and the NaCl values in the blood lay at the upper level of normal values, but tended to drop as the anemia improved. The CO₂ tension in the blood was decreased and rose with improvement of the anemia. In the cases coming to autopsy the kidneys showed slight or no pathological changes, indicating that the process was functional rather than anatomical. Low blood pressure was ruled out as a cause as no blood pressures below 95 were obtained. It is probable that in anemias the insufficient supply of O brought to the kidney, through lowering of the hemoglobin content of the blood, leads to a functioning of the kidney on the plane calling for the least expenditure of energy, that is the secretion of a urine isotonic with the blood. The edema may be explained by injury to the capillary walls through asphyxia, rendering them more pervious.

HARRIET F. HOLMES

Immunological experiments with platelets of human blood. F. R. MENNE. *J. Infectious Diseases* 31, 455-60(1922).—The platelets were obtained by fractional centrifugation of human blood. Suspensions of platelets when injected into rabbits gave rise to precipitins; agglutinins, lysins and opsonins for platelets. The results of the precipitin test point to a definite difference in the constitution of the platelets and leucocytes in human blood.

JULIAN H. LEWIS

Influence of saturation on properties of antigen in the Wassermann test. C. I. A. SCHMIDT AND S. E. COFFEY. *J. Infectious Diseases* 32, 119-23(1923).—Satn. of the alc.-sol. and acetone-insol. lipid commonly used as the antigen in the Wassermann test for syphilis was accomplished with the aid of the method described by Pool. Both the unsatd. and the hydrogenated lipid prepn. are capable of acting as antigens in the Wassermann reaction. The hydrogenated lipid prepn. is distinctly more anti-alexig (anticomplementary) than the untreated antigen

JULIAN H. LEWIS

A modified toxin-antitoxin mixture. W. BIEBER. *Centr. Bakt. Parasitenk.*, I Abt. 89, 143-7(1922).—A prepn. of toxin with the minimum amt. of antitoxin produces the best immunization to diphtheria. A toxin that is made neutral for a guinea pig with antitoxin is still toxic for man. B. uses a prepn. that is slightly overneutralized for guinea-pigs.

JULIAN H. LEWIS

Immunological analysis of the complex structure of serum proteins. R. DOERR AND W. BERGER. *Z. Hyg. Infektionskrankh.* 96, 191-215(1922).—Four proteins isolated from blood serum were studied as to their ability to act as anaphylactogens and as to their specificity. Euglobulin was obtained by $\frac{1}{3}$ satn., pseudoglobulin by $\frac{1}{2}$ satn., albumin C by 66% satn., and albumin D by complete satn. with (NH₄)₂SO₄. Guinea pigs sensitized with euglobulin were not sensitive to albumin. The 2 albumins showed a difference in specificity. Euglobulin also differed from albumin in what is called its biol. activity. The minimal sensitizing dose and the incubation period were smaller for euglobulin than albumin. Arranged in order of their biol. activity they are euglobulin, pseudo globulin, albumin C and albumin D. The specificity of these proteins depends on the chem. structure rather than the colloidal properties. Theories are given of the relation of species specificity of serum to the chem. specificity of the constituent proteins, to their antigenic activity and to the mutual antigenic antagonism which results in immunization to more than one protein.

JULIAN H. LEWIS

The catalase content of blood and its significance for differential diagnosis. E.

SEGALL AND M. HANDEL. *Deut. Arch. klin. Med.* 138, 243-8(1922).—The catalase figures obtained in Austria are smaller than those obtained by van Thienen in Germany. This is due to the use of a different method and to the different food conditions existing in Austria. The catalase value for women is less than that for men. There is a reduction of the catalase figure in any disease in which there is cachexia. In anemias, especially pernicious anemia, there is a reduction of catalase even though there is no cachexia. The catalase index is obtained by dividing the red cell count by 1,000,000 and dividing the catalase figure by the quotient. In pernicious anemia this index is many times, but not constantly, abnormally increased. Other anemias also may cause an abnormally high catalase index. There is no agreement with van Thienen that pernicious anemia may be diagnosed by the catalase index.

JULIAN H. LEWIS

The theory and practice of foreign protein therapy. A. SCHITTENHELM. *Centr. Bakt. Parasitenk.*, I Abt. 89, 90-4(1922).—A review of the use to which the parenteral administration of foreign proteins has been put.

JULIAN H. LEWIS

The relation between temperature and complement action. W. BENDER AND C. PRAUSNITZ. *Centr. Bakt. Parasitenk.*, I Abt. 89, 219-24(1922).—Artificially increased temp. produced by exposure of men and rabbits to high outside temps. caused a decided increase of the complement titer. *In vitro* hemolysis is increased at 40° but this is due to the lability of the red corpuscles. There was no way to tell if complement was more active at 40°.

JULIAN H. LEWIS

The effect of thyroidectomy, controlled by respiratory exchange measurements, on antibody formation in rabbits. N. M. TAKÉ. *J. Infectious Diseases* 32, 138-43 (1923).—Thyroid insufficiency, detd. by heat production measurements, does not inhibit or increase the hemolysin and agglutinin (typhoid) formation in rabbits.

JULIAN H. LEWIS

Studies on complement fixation. VI. The velocity of fixation of complement with bacterial antigens. R. L. KAHN AND S. R. JOHNSON. *J. Infectious Diseases* 31, 416-25(1922).—The velocity of fixation of complement at ice-box, room and water bath temps. was studied with the following 6 antigen-antibody complexes: *B. abortus* with bovine serum, *B. typhosus*, *B. paratyphosus* A and B, *B. mallei* and *B. pullorum* with sp. rabbit serum. The fixation periods in each case were 0, 5, 15 and 30 min. and 1, 2, 3, 4, 5, and 6 hrs. The velocity of fixation of complement is practically the same at different temps. studied with all organisms except *B. pullorum*. With this organism fixation at water bath temp. was more marked than at ice-box and room temps. With the exception of *B. pullorum*, a fixation period of 4 hrs. at ordinary ice-box temp. is superior to a 1-hr. period in the water bath. This period of fixation in the water bath was of insufficient length to bring about complete fixation of complement with 5 of the organisms studied. Furthermore, the employment of water-bath temp. for fixation of complement should be avoided as far as possible because this temp. hastens the deterioration of complement. The mode of fixation of complement with a given bacterial antigen should be detd. by special "titration" in the same way that various other factors of the complement-fixation test are detd. by titration. The numerous ways of prepg. bacterial antigens combined with the varying complement fixation procedures employed by different workers necessitates this step until more is learned of the laws governing the phenomenon of complement fixation. A simple outline is given for detg. the optimum temp. and time of fixation of complement with different bacterial antigen-antibody complexes. VII. The determination of the optimum amount of antigen in complement fixation tests. *Ibid* 426-37.—See C. A. 17, 308. VIII. The effect of inactivation on complement fixing substances in syphilitic serum. *Ibid* 438-43.—The inactivation of syphilitic serum for 1/2 hr. at 56° enhanced the complement-fixation reaction in many cases, providing the period of fixation was no less than

4 hrs. at ice-box temp. A small loss in antibody content following inactivation was observed in some cases. The proportional antibody gain, however, due to inactivation, was greater than the antibody loss.

JULIAN H. LEWIS

A comparative study of precipitinogen and precipitin curves with especial reference to the later history of the precipitin curve. G. F. FORSTER. *J. Infectious Diseases* 32, 105-18(1923).—With sheep serum as an antigen, the precipitinogen disappearance curve, the precipitin curve, and the interrelations of the 2 have been studied in 14 rabbits. When doses totalling 20-30 cc. were administered on the 1st, 3rd and 5th days, precipitinogen disappeared from the circulation in an av. time of 7.25 days after the last injection. Precipitin production, with the same dosage, began invariably within 1-3 days, and reached its crest in an av. time of 10.3 days. This time, as well as that required for the elimination of precipitinogen, is probably somewhat longer than the normal, for the reason that after a period of from 30 to 50 days the antibody curve does not continue to pursue a steady downward path, but evidences a modified behavior: 1st, the curves representing the ring test and the flocculation test diverge markedly, the ring test curves persisting much longer than the flocculation curves; 2nd, soon after this period is entered on, the flocculation ceases to occur in the lowest dilns., although still occurring in higher dilns.; furthermore, the lower limit of flocculation rises with successive titrations, while the upper limit falls; therefore, curves representing the upper and lower limits of flocculation converge. This is also characteristic of the ring test, but the altered behavior of the latter does not begin for some time after that of the flocculation test. Three pairs of curves thus are shown in graphs illustrating this later history of the antibody, representing the upper and lower limits of pptn. in the 3 following tests: (1) ring test, after 20 mins.; (2) flocculation test, after 2 hrs.; (3) flocculation test, after 18 hrs., when pptn. is complete. The curves for the ring test persist long after both flocculation tests have become negative. The 2-hr. flocculation curve ends soon after the period of modified behavior begins (within 5-20 days thereafter). The 18-hr. curve continues 50-80 days after this period has begun. The ring test curve has not yet ended in any case studied, although one has been followed for 287 days after the beginning of this period.

JULIAN H. LEWIS

The back-flow of pancreatic juice into the stomach and the acid resistance of trypsin. G. DRUSCH AND H. RÜRUP. *Deut. Arch. klin. Med.* 138, 165-74(1922).—The limit of resistance of trypsin to HCl is about 0.05% HCl at body temp. At this concn. trypsin is destroyed in 3-5 mins. The free HCl alone is active in destroying trypsin. These facts preclude the possibility of tryptic digestion occurring in the stomach except in achlorhydria or hypochlorhydria. They prevent trypsin serving as an indicator of the back-flow of pancreatic juice into the stomach. The tests of pancreatic function which are based upon stomach content analyses are made invalid.

JULIAN H. LEWIS

The relation of fraction specificity to species specificity of proteins of blood serum. R. DOERR AND W. BERGER. *Z. Hyg. Infektionskrankh.* 96, 258-62(1922).—Each of the proteins tested (euglobulin and albumin) possesses a double specificity, fraction specificity and species specificity. In each mol. of these proteins there exist 2 independent but distinct groups upon which depend the kinds of specificity. The proteins isolated by pptn. with $(\text{NH}_4)_2\text{SO}_4$ are not artefacts but are the same proteins which circulate in the blood stream, because the intoxicating dose of a protein is the same either given in its pure form or unisolated in blood serum.

JULIAN H. LEWIS

The reliability of the Sachs-Georgi test for syphilis. J. W. RICE. *J. Infectious Diseases* 31, 444-54(1922).—When roughly classified into "positive" and "negative," the Sachs-Georgi tests agreed with the Wassermann tests in 94.4% of 1,000 cases tested. The Sachs-Georgi test appears to be less sensitive than the Wassermann reaction in patients receiving antisyphilitic treatment and in cases of cerebrospinal syphilis. The

Sachs-Georgi test is just as sensitive as the Wassermann test in untreated cases of primary, secondary and tertiary syphilis. The specificity of the Wassermann alc. antigen under the 4-hr. icebox treatment can be questioned when the presence of bile salts in the patients serum is ignored. With this unknown quantity controlled, the Sachs-Georgi test would show a still more favorable comparison with the Wassermann reaction as a routine test. In each of 4 cases in which the patient's serum was anticomplementary in the Wassermann test, the Sachs-Georgi test gave a definite and reliable diagnosis. Because of the simplicity and reliability of the test, as shown by the data presented, the Sachs-Georgi test should attain a range of usefulness in the diagnosis of syphilis far in excess of that accredited to it at the present time.

JULIAN H. LEWIS

The significance of the conglutination and K-H reactions in the diagnosis of glanders. K. POPPE. *Centr. Bakt. Parasitenk., I Abt.* 89, 29-48(1922).—Normal inactivated beef serum in the presence of fresh horse serum as complement has the ability of agglutinating red cells from the sheep. This phenomenon is called conglutination. Since complement is necessary for the reaction it can be used as an indicator for the fixation of complement. Normal inactivated beef serum has also the property of hemolyzing red cells from the guinea pig when horse serum complement is present. When complement is absent the guinea pig red cells are agglutinated. This reaction is called the K-H reaction and can also be used to detect complement fixation. P. found these 2 reactions useful in the diagnosis of glanders. In 2729 horses suffering from this disease, the conglutination reaction was positive in 93.3%, and in 2419 such horses the K-H reaction was positive in 94.3%. These reactions showed greater constancy than the original complement-fixation reaction.

JULIAN H. LEWIS

Specific precipitin reaction of semen. LUDVIG HERTOEN AND L. S. MANLEY. *J. Infectious Diseases* 32, 167-71(1923); cf. *C. A.* 16, 2705.—The injection of rabbits with human semen, with human seminal fluid, or with ext. of human spermatozoa induces the formation of precipitins that are sp. for human seminal proteins. The seminal precipitin reaction promises to be of value in detg. the nature of suspected seminal spots and stains. Swine, bovine and equine seminal fluids injected in rabbits also lead to the production of species and semen-sp. precipitins. Serum precipitins in antiserum for serum may be removed by selective absorption with the proper serum in a 1:200 diln. The precipitin reaction may be of value in the study of the constituents of the sex cells.

JULIAN H. LEWIS

The influence of the technic and other factors on the titer of hemolytic amboceptor. H. DOLD AND G. KLINGHART. *Arb. Staatsinst. Exptl. Therap.* 1922, No. 15, 23-33.—The unaccountable variations in the results of daily titrations of the same hemolytic amboceptor led to a study of the factors which might be of influence. Fresh guinea pig serum shows marked variation in its complement action during the first hrs. after it is obtained. Usually during the 1st 4 hrs. there is a sudden drop in its titer and a rise to normal during the next 2 hrs. Changes in titer which occur later appear gradually. Undil. guinea pig serum kept at 37° for 1-4 hrs. undergoes no appreciable change in titer. Direct sunlight after 4 hrs. exposure is harmful to complement. Shaking 3-10 min. has no effect. Shaking undil. amboceptor 20 hrs. has no effect. The kind of glass in which amboceptor is stored has no effect on its titer. Any variation from neutrality of the physiol. NaCl soln. used in making dilns. of amboceptor causes considerable decrease in the titer. Small amts. of acid are more harmful than small amts. of alkali. The technic of making dilns. of amboceptor may greatly influence the results. The pipet used for making low dilns. should not be used for making high dilns. In measuring concd. amboceptor with a pipet account should be taken of the drainage on the outside of the pipet.

JULIAN H. LEWIS

The influence of technic and other artificial factors on the titration value of hemo-

lytic amboceptors. H. DOLD AND G. KLINCKHART. *Arb. Staatsinst. Exptl. Therap.* 1922, No. 15, 21.—Fresh guinea-pig serum shows in the first hours after it is obtained marked variation in its complement activity. Most frequently the titer is high at first, falling within the first 4 hrs. sometimes to $1/4$ of the original value, then returning to the original titer perhaps within the next 2 hrs. Less often the titer at first is low and rises gradually to the max. height. In later periods such marked variations are not observed. Preservation of the undild. serum at 37° for 1 to 4 hrs. causes no considerable reduction in the titer. Direct sunlight has an injurious effect after about 4 hrs. Shaking of undild. amboceptor in the shaking machine for even 20 hrs. has no distinctly injurious effect, which indicates that the shaking of serum in transportation cannot be harmful. The sort of glass used for contg. amboceptors was also without influence in a 9 weeks expt. The reaction of the salt soln. used for dilg. the serum is very important, acidity having an even more markedly injurious effect than corresponding increase in alkali. The technic of the diln. may have an influence on the titer, strong shaking or blowing through the serum or repeated changes of pipet all reducing the titer.

H. C. WELLS

Wassermann and flocculation tests compared in 1000 cases. A. L. URQUHART. *Lancet* 1923, I, 125-8.—The flocculation reaction is as reliable as the Wassermann and preferable on account of its simplicity. Sheep heart ext. makes satisfactory antigen. Contamination or hemolysis in the sera may cause false positive readings; sera so affected must not be used. Bile pigment and an anticomplementary state of the serum do not interfere with the test.

E. R. LONG

The interpretation of blood sugar estimations that are near the normal. H. J. JOHN. *J. Lab. Clin. Med.* 8, 145-52(1922).—Several cases are described in which no glucosuria occurred, where blood sugar was normal or slightly above normal, but where glucose tolerance was low and a typical diabetic curve of sugar excretion followed glucose administration. The patients were considered mild diabetics and treated accordingly.

E. R. LONG

The quantitative flocculation test for syphilis. A comparison of 500 cases with the Wassermann, using a simplified Sachs-Georgi technic. H. M. FEINBLATT. *J. Lab. Clin. Med.* 8, 200-6(1922).—Parallel Sachs-Georgi and Wassermann exams. (500) showed an agreement of 93.8%. Of the 31 conflicting cases 16 were positive to the Sachs-Georgi and 15 to the Wassermann. Of the 16 reacting positively to the Sachs-Georgi, 15 presented definite clinical evidence of syphilis. Of the 15 reacting to the Wassermann, but negatively to the Sachs-Georgi, 11 had clinical evidence of syphilis.

E. R. LONG

Colloids, catalysis, antigens, antibodies. M. NICOLLE AND E. CÉSARI. *Ann. inst. Pasteur* 36, 463-93(1922).—A résumé. Previously 2 types of antibodies have been considered to exist: (1) a coagulating, including agglutinins, precipitins and antitoxins, and (2) lysins, including cytolytins, the sensitizing substance of Gengou and the toxinolysins. It is decided to abandon this classification. Every antigen provokes the formation of 1 sp. antibody; in the absence of complement the action is coagulating; in its presence decoagulation succeeds coagulation.

E. R. LONG

Antigenic value of tubercle bacilli and other bacteria grown on egg media. A. URBAIN. *Ann. inst. Pasteur* 36, 528-33(1922).—Of a group of microorganisms grown on the medium of Besredka human type tubercle bacilli had the greatest antigenic value, the diphtheria bacilli and certain paratubercle bacilli somewhat less, and the hay bacillus, the staphylococcus and streptococcus none at all. Four-day cultures give the highest antigenic value. The liquid part of the culture enriches with age, while the bacilli lose. Antigen prepd. from egg media loses none of its activity after 15 months preservation.

E. R. LONG

Attempts to vaccinate the rabbit and guinea pig against tuberculous infection. A. CALMETTE, L. NEGRE AND A. BOQUET. *Ann. inst. Pasteur* 36, 625-32(1922).—Inoculation of guinea pigs and rabbits with tubercle bacilli attenuated with bile confers a resistance of only short duration, ceasing in 5-6 months with the elimination or absorption of the bacilli. E. R. LONG

The abolition of function of the alcoholic beef heart extract by cobra toxin, and its significance for the theory of the Wassermann reaction and the Sachs-Georgi flocculation reaction. E. NATHAN. *Z. Immunitäts.* 35, 392-406(1922).—The treatment of alc. beef heart ext. with cobra toxin robs the ext. of its ability to react with syphilitic sera by complement adsorption or flocculation. The inhibitory effect on both reactions indicates that the same constituents of the ext. are involved in the 2 reactions, and the destruction of these constituents by lecithinase shows their lipid nature. Treatment of completely flocculated ext.-serum mixts. with cobra venom occasionally causes a disappearance of the flocculate. The reaction between ext. and syphilitic serum is thus not of the type of a fixed, irreversible combination. E. R. LONG

Comparative researches on the curative action of high titer and low titer antidiphtheria serum. KAZUFUSA SATO. *Z. Immunitäts.* 35, 344-65(1922).—Only the antitoxin content of antidiphtheria sera plays a role in curing diphtheria. The result is independent of the quantity of serum injected with the antitoxin. E. R. LONG

Anaphylaxis and immunity. S. METALNIKOW. *Ann. inst. Pasteur* 36, 632-45 (1922); cf. C. A. 16, 4266.—Cellular hypersensitivity is at the basis of both immunity and anaphylaxis. It is expressed by a marked reaction on reintroduction of antigen, in which all cells (fixed and wandering) may react, including those of the blood vessels and nerves. Anaphylaxis is the result of rapid reactions of cells sensitized by immunization. Local anaphylaxis follows subcutaneous inoculation; general follows intravenous inoculation. E. R. LONG

The influence of the salt content on the Wassermann reaction with active serum. SEIGO KONDO. *Z. Immunitäts.* 35, 366-92(1922).—The Wassermann reaction (W. r.) with active serum becomes positive with almost every serum if the salt content is greatly decreased. The anticomplementary action of the ext. and patients' serum is also strengthened, as is the so-called alc. reaction, which depends on the alc. of the ext. The alc. acts as a weak globulin-pptg. material, acting especially on labile sera. The ext. lipoids act apparently in the same manner. In the W. r. and the flocculation reaction ext. constituents react with the active serum in the manner of an insulation with labile proteins. Under the conditions of the W. r. this leads to an anticomplementary function of the altered globulin. The process is checked by salt excess. In the W. r. 0.85% NaCl exerts an antagonism to the anticomplementary action. E. R. L.

Intestinal antiseptics. Effect of antiseptics on a type of experimental intestinal toxemia. L. R. DRAGSTEDT, C. A. DRAGSTEDT AND O. M. NISBET. *J. Lab. Clin. Med.* 8, 196-3(1922).—Death from acute intestinal obstruction is due to toxemia. The toxic materials are produced by the action of the normal intestinal bacteria on the intestinal contents. The symptoms can be produced in dogs by the production of closed, isolated segments of various parts of the small intestine. If the segment is removed symptoms disappear. The production of such closed segments afforded an opportunity for testing the efficiency of intestinal antiseptics. Alc., ether, 2% lysol, 5% AgNO₃, satd. ZnCl₂, 5% C₆H₅OH, satd. salol, 10% thymol in alc., solid camphor, solid menthol, naphthalein, Dakin soln., β -naphthol, satd. quinine sulfate and HgCl₂ (strength not stated), directly applied to the short segments, did not cause sterilization or inhibit the production of intestinal poisons. E. R. LONG

Hepatic reactions in anaphylaxis. I. Vaso-motor reactions in the isolated canine liver. W. H. MANWARING AND SELLING BRILL. *J. Immunol.* 8, 47-53(1923).—Simonds'

theory as to the fundamental nature of the reaction in canine anaphylaxis was tested by perfusion methods with isolated tissues. Distinct vasoconstriction can be demonstrated in the canine lungs by perfusion with a mixt. of BaCl_2 and adrenaline chloride, and marked vasoconstriction by perfusion with ergotin or with Vaughan's protein split product. No venoconstriction can be demonstrated in canine livers, however, by perfusion with any of these agents. Simonds' hepatic veno-constrictor theory, therefore, does not appear to represent a physiol. possibility. E. R. LONG

The relation of antigen to antibody (precipitin) in vitro. E. L. OPIE. *J. Immunol.* 8, 19-34(1923).—Excess of antigen dissolves the ppt. formed by the action of precipitin and its antigen. Inhibition of sp. pptn. (inhibition zone) in the presence of high concn. of antigen is caused by the solvent action of excess of antigen. Proteins of the blood serum do not prevent pptn., and the reaction has the same characters whether dilns. of antigen and antibody are made in salt soln. or in normal blood serum. When a const. quantity of antigen is mixed with increasing quantities of immune serum the max. amt. of ppt. is found when antigen is mixed with several hundred times its vol. of immune serum, the number of vols. depending on the strength of the serum. An excess of antigen added to the mixt. becomes demonstrable in the supernatant fluid. This relation furnishes a measure of the strength of the immune serum detd. in multiples of the vol. of the antigen used for the test. The presence of antigen and antibody in the supernatant fluid over a ppt. obtained by adding to the antigen (horse serum, egg white, etc.) an amt. of antibody in excess of that required to produce the max. amt. of ppt. is best explained by the assumption of a multiplicity of antigens in such complex mixts. as blood serum and egg white. Cryst. egg albumin is an almost pure antigen, but contains in very small amt. extraneous antigen capable of forming precipitin.

E. R. LONG

The relation of antigen to antibody (precipitin) in the circulating blood. E. L. OPIE. *J. Immunol.* 8, 55-74(1923).—Antigens such as horse serum or egg white injected into a normal animal are demonstrable in the blood during approx. 7-9 days after injection; antigen disappears shortly after the appearance of precipitin at a time when the concn. of precipitin is rapidly rising. In exceptional instances antigen persists during a much longer period, e. g., 19 days, and in these animals formation of precipitin proceeds slowly and their concn. in the serum remains low. With the progress of immunization, injected antigen exhibits a decreasing tendency to find its way into the circulating blood, so that in a well immunized animal horse serum or egg white injected into the subcutaneous tissues is not demonstrable in the blood serum, even if tests are made at intervals from 1 to 24 hrs. after injection. Complex antigens, such as horse serum or egg white, injected into an immunized animal cause a diminution of the concn. of precipitins, but precipitins do not disappear completely and in the early stages of immunization both antigen and antibody may be demonstrable in the same serum. A simple antigen, viz., cryst. egg albumin, purified by repeated crystn., injected into an animal immunized against this substance may cause temporary but complete disappearance of precipitin, and, though antigen may appear in the serum, in no instance has this antigen and its precipitin been found simultaneously in the serum. These observations on living animals, like the coexistence of antigen and antibody without a ppt. *in vitro*, are explained by the presence of multiple antigens in mammalian serum or in egg white and a corresponding multiplicity of antibodies in immune sera. The behavior of precipitins in the living body is similar to that in the test-tube, and indicates that they ppt. foreign protein introduced into the immune animal. E. R. LONG

Hemolytic action of venoms from various South American snakes. B. A. HOUSSEY AND J. NEGRETE. *Compt. rend. soc. biol.* 87, 828-30(1922).—A detailed account of a comparative study of the hemolytic activity of various venoms as well as sensitivity of red blood cells from different organisms. S. MORGULIS

The cholesterolemia of subjects suffering from arteritis obliterans. JEAN HEITZ. *Compt. rend. soc. biol.* **87**, 1024-6(1922).—In 22 patients with arteritis obliterans but showing no symptoms of diabetes the cholesterol content of the blood was higher than normal; the av. was 0.282 g. per 100 cc. blood (with only one detn. less than 0.2 and 9 with more than 0.3 g.) in place of 0.16 g. taken as the normal. None of the cases examd. showed any signs of Bright's disease, syphilis or biliary calculi, and their blood pressure was normal. S. MORGULIS

Formalin gelification of serums from tuberculous cattle. L. PANISSET AND J. VERGE. *Compt. rend. soc. biol.* **87**, 667-9(1922).—The authors conclude that the formol reaction of Caté-Papacostas is not sp. and cannot be employed as a diagnostic sign for tuberculosis in cattle, though they do not wish this conclusion to be understood to apply to other pathol. conditions. S. MORGULIS

The gelification of plasma with formaldehyde. E. NICOLAS. *Compt. rend. soc. biol.* **87**, 669-71(1922).—Fibrinogen does not play an important role in the gelification of plasma, the essential factor in the reaction being the serum-globulin. The action of formaldehyde on solutions of fibrinogen. *Ibid.* 671-2.—Fresh solns. of fibrinogen which are coagulable by thrombin can be gelified with HCHO. If, however, the soln. is old and is no longer coagulable by thrombin (though it gives a ppt. with NaCl) the HCHO also fails to produce an effect. Furthermore, such a fibrinogen soln. after the HCHO had been added to it is well stabilized and is not pptd. by heating to 56 or even 75°. S. MORGULIS

Comparative development of tuberculosis in guinea pigs on a normal and on a deficient diet. G. MOURIQUAND, PAUL MICHEL AND P. BERTOYE. *Compt. rend. soc. biol.* **87**, 854-6(1922).—Scurvy develops with the same intensity in normal as in tuberculous animals. Under the influence of the Koch bacilli the same amt. of antiscorbutic substance is necessary for relief as in healthy guinea pigs. S. MORGULIS

Anaphylaxis in a series of animals. Experimental anaphylactic shock in pigeons. F. ARLOING AND L. LANGERON. *Compt. rend. soc. biol.* **87**, 632-4(1922).—Anaphylaxis can be induced also in birds (pigeons) through the injection of foreign serum. Peritoneal injection is more effective than intravenous injection in causing sensitization and shock. Apparently 5 cc. of serum is sufficient to produce the effect. This expresses itself in the usual nervous and motor phenomena and an hemoclastic crisis with typical leucopenia. **Amphibia and fishes.** *Ibid.* 634-5.—Expts. in which horse serum was used to sensitize frogs and various species of fish were all entirely negative. S. MORGULIS

Anti-gangrene serum. A. SORDELLI. *Compt. rend. soc. biol.* **87**, 1052-3(1922).—The toxin produced by putrefactive germs, cultured in a 2% peptone bouillon at pH 8, and obtained by filtering, is so active that 0.001 cc. intramuscularly is sufficient to kill a 250 g. guinea pig. If the animal does not die within 2-3 days it usually survives a long time but develops an extensive edema. With this toxin a horse was immunized for 1½ month. 0.001 cc. of the immune serum was enough to neutralize 0.5 cc. of the toxin (filtrate from a 5-day old culture); 0.0003 cc. serum retarded death 10 days. The serum neutralizes also the infection caused by the organism and can be recommended in treatment of gangrene where this organism (*B. oedematiens*) is present. The serum is ineffective against *B. perfringens* or septic vibrio. S. MORGULIS

Physico-chemical changes in the blood at the time of injection of serum treated with agar. EDGARD ZUNZ AND JEAN LA BARRE. *Compt. rend. soc. biol.* **87**, 805-7 (1922).—Injection of guinea-pig serum treated with agar according to Bordet's method into guinea pigs has an effect upon the blood similar to that produced by injections of horse serum into previously sensitized guinea pigs; there is an increase in the red cells; the viscosity is raised but that of the plasma is unaffected; the coagulation capacity is diminished; the π is increased and the surface tension is lowered. These alterations

do not appear if the guinea pig receives a preliminary injection of hirudin and is thus protected against the injurious influence of the agar treated serum. Serum heated to 58° for 20-30 min. before treatment with agar no longer causes these changes.

S. MORGULIS

Potassium in the blood serum in renal insufficiencies. D. OLMER, L. PAYAN AND J. BERTHIER. *Compt. rend. soc. biol.* 87, 867-9(1922).—From analyses the authors conclude that in subjects with a normal non-protein N there is scarcely ever any evidence of an increase in the amt. of K, and the level of the latter in the serum is not parallel to the curve of N retention. Although a high K content of the serum may be associated with toxic symptoms, either of nervous origin, or muscular, cardiac or blood itself, a survey of the results obtained with subjects suffering from renal insufficiencies fails to disclose any relationship. The high K level apparently plays no important role in the uremic condition.

S. MORGULIS

Colloidal equilibrium of serums from normal and pathological bloods. ROGER FISCHER. *Compt. rend. soc. biol.* 87, 958-61(1922).—The globulin exercises a protective action on albumin and to this relationship of the 2 proteins resulting in an equil. state is applied the name *prostasy*. Serum is obtained by allowing 10 cc. of blood from a vein to clot spontaneously. 0.3 cc. of the serum is used in the test, which consists in detg. the pptg. effect of alc. on gelatin in the presence of the serum. A dis-equilibration in the colloids of the serum apparently does not occur except in diseased individuals approaching a fatal termination.

S. MORGULIS

Digestive hemoclasia resulting from the ingestion of proteins as a means of studying hepatic insufficiency. MANUEL FERNANDES. *Compt. rend. soc. biol.* 87, 706-7(1922).—Hemoclasia rarely fails to appear as a result of the ingestion of 200 cc. of milk. The most marked and const. sign of this hemoclastic crisis is the leucopenia which, however, should be looked for not later than 40 min. after the ingestion of milk. There was no const. relation between the degree of leucopenia and the gravity of the hepatic lesion, while the absence of leucopenia does not exclude the possibility of liver trouble. Next in importance to the leucopenia is the increase in coagulability of the blood.

S. MORGULIS

Autolysis in persons suffering from cancer. FÉLIX RAMOND AND PIERRE ZIZINE. *Compt. rend. soc. biol.* 87, 657-8(1922).—The total N and urea N were detd. in the blood of 2 subjects following deproteinization with $\text{CCl}_3\text{CO}_2\text{H}$ or with metaphosphoric acid. The difference in the total N obtained by these 2 pptn. methods is regarded as polypeptide N. According to the blood analyses the polypeptide N is greatly increased in persons with cancer, and this fact is considered further evidence that the autolytic processes are much augmented.

S. MORGULIS

The calorific coefficients for babies with congenital syphilis. MANICATIDE, A. STROE AND PAIS. *Compt. rend. soc. biol.* 87, 732(1922).—Such babies have a much higher calory requirement than normal babies of the same age. In 50% of the cases up to 220 Cal. per kg. was needed to secure normal development. In 31% of the cases results were obtained only after the calories of the milk were augmented through the addn. of sugar to 148 Cal. per kg. In 6% of the cases the liberal supply of calories in the food proved of no avail and the babies died of cachexia.

S. MORGULIS

Parotid stone in man. Chemical examination of a stone spontaneously evacuated from the duct. L. DEBUCQUET. *Compt. rend. soc. biol.* 87, 1079-81(1922).—The parotid calculus was small and round, weighing 0.012 g. It gave negative results in tests for cholesterol or uric acid. The center of the stone was of Ca which was the predominant component but it, also gave the xanthoproteic protein test.

S. M.

Hemoclastic shock in epilepsy. J. TUDORAN. *Compt. rend. soc. biol.* 87, 743-4(1922).—Hypoleucocytosis with lowering of arterial pressure was observed in 12 cases;

23 other cases showed considerable hyperleucocytosis with much greater drop of pressure (1 to 4 cm.); in 2 cases leucopenia was observed together with a rise in blood pressure and in 2 other cases the same occurred with a hyperleucocytosis, and in 3 cases no variations in pressure were noted at all.

S. MORGULIS

Alimentary leucopenia in pregnant women. S. MAZZA AND D. IRAETA. *Compt. rend. soc. biol.* **87**, 691(1922).—In 36% of 44 cases of pregnancy investigated the ingestion of 200 cc. of milk on the empty stomach produced leucopenia. A diminution of less than 2000 white cells per cu. mm. was not regarded as significant. The leucopenia was more frequent among the primiparas than those with the second pregnancy. Also in the puerperal period the alimentary leucopenia could be produced and occurred with much greater frequency among the primiparas.

S. MORGULIS

Refractometric index of the serum of pregnant females and its variation during the hemoclastic crisis. S. MAZZA AND D. IRAETA. *Compt. rend. soc. biol.* **87**, 690(1922).—The n of the serum of a number of primiparas varied between 1.3536 and 1.34798, and only in 2 out of 16 did the ingestion of milk bring about a slight diminution. No relation was found to exist between alimentary leucopenia and the change in n .

S. M.

Sedimentation of the red blood cells and pregnancy. H. VIGNES AND P. HERMET. *Compt. rend. soc. biol.* **87**, 952-3(1922).—The rapid sedimentation of the red cells becomes the more marked the more advanced the pregnancy and is thought to be in correlation with the destruction of substances in the mother's organism occasioned by the fetus. The reaction disappears in the post-partum or post-abortion state but with a variable rate. It is not due to change in the sp. gr. of the plasma, and addn. of H_2O *in vitro* or of physiol. serum had no effect on the rate of sedimentation. The reaction is considered as resulting from some modification in the chem. constitution of the plasma and more particularly of its colloidal materials. By adding various substances, as serum from men and from women both pregnant and non-pregnant, it was only the serum from pregnant women that showed a definite and striking influence on the sedimentation of the red cells.

S. MORGULIS

Serological researches on protozoa. I. Morphology and serological properties of Prowazekia (Bodo) edax. LUDWIK ANIGSTEIN. *J. Trop. Med. Hyg.* **25**, 241-6 (1922).—An immunological study of the intestinal flagellate Prowazekia (or Bodo). Immune serum was produced in rabbits and frogs. The immune serum showed no sp. lysins, but did show the abundant presence of agglutinins and of complement fixing antibodies.

W. A. PERLZWEIG

Pancreatic diabetes in the dog. VI. The influence of pancreatic extracts without the aid of alkali upon the metabolism of the depancreatized animal. J. R. MURLIN, BENJAMIN KRAMER AND J. E. SWEET. *J. Metabolic Research* **2**, 19-27(1922).—The details of expts. performed in 1913-16 (cf. *C. A.* **11**, 359, 360, 482) are presented which confirm the recent findings of Banting and Best (*C. A.* **16**, 1980, 2905) concerning the presence in pancreatic tissue of a substance capable of restoring to the diabetic animal the ability to utilize glucose.

W. A. PERLZWEIG

Experimental studies in diabetes. IV. Lipemia. I. Analyses of blood lipoids in diabetic animals and patients. M. B. WISHART. *J. Metabolic Research* **2**, 199-217 (1922); cf. *C. A.* **16**, 2364.—“The name *lipemia* is justified by the fact that neutral fat is the principal substance which accumulates in the blood. The higher the lipemia, the higher is the ratio of the glycerides to other lipoids such as lecithin and cholesterol. The quant. excess of fatty substances is the chief cause of the milky turbidity of the plasma. The analyses confirm, however, the statement of former writers that samples of plasma contg. a marked excess of fat may be clear, while others contg. much less fat may be turbid. No definite relations have been found between the various lipoids to explain these differences. The analyses show that the ratios between the different

lipoids are subject to wide variations. The combination of active severe diabetes and a high fat diet is undoubtedly most conducive to lipemia. Some degree of lipemia, however, may be reckoned among the most stubborn symptoms of severe diabetes, and may persist for at least several weeks after the disappearance of both hyperglucemia and acidosis, on diets very low in fat and total calories. Diets high or low, resp., in cholesterol or lecithin have shown no decisive influence in either producing or clearing up lipemia. Diabetic patients and animals, known to be subject to lipemia, have not shown any remarkable retention of cholesterol in the blood when fed cholesterol or cholesterol-rich foods. No uniform parallelism has been found between the sugar or acetone in the blood or urine and the accompanying degree of lipemia. The same is true of the CO₂ capacity of the plasma. Also, the giving of carbohydrate or its exclusion from the diet seems not to be a detg. factor in lipemia. The observations with alc. are suggestive but incomplete. When active diabetic symptoms are restored by an excessive caloric diet composed essentially of protein, carbohydrate and alc., a definite but moderate lipemia results as one of the active symptoms. It is undecided whether alc. has any sp. influence in lowering lipemia, comparable to its occasional temporary action in reducing hyperglucemia and glucosuria." The above conclusions are based on an unusually large series of analyses on whole blood, plasma and corpuscles of exptl. animals and diabetic patients including figures for total fat, cholesterol, lecithin, total fatty acids and glycerides. II. The production of diabetic lipemia in animals, and observations of some possible etiologic factors. F. M. ALLEN. *Ibid* 219-98.—A very extensive review is given of the literature of lipemia and fat metabolism. The bibliography contains 377 references, and a short abstr. accompanies each reference. On the basis of his own expts. A. concludes that: "Severely diabetic dogs which digest high fat diets regularly develop some degree of abnormal lipemia, and in a minority of such animals this lipemia becomes extreme (15% or more of blood fat). The chief positive result of this investigation is the establishment of a complete similarity between clinical and exptl. diabetes in regard to lipemia. Apart from a sufficient supply of fat in the diet the one indispensable prerequisite for diabetic lipemia is the existence of active severe symptoms in the form of glucosuria and hyperglucemia. Mild cases with high glucosuria and severe cases with glucosuria abolished by diet never exhibit any extreme grade of lipemia, however high the fat intake. Diabetic lipemia evidently represents some secondary breakdown in fat metabolism, not directly connected with the endocrine function of the pancreas and not due merely to excess of fat in metabolism or loss of sugar from the body. There are wide variations in individual susceptibility to this disorder among both animals and patients. Tests with a wide variety of endocrine, dietary and other influences failed to reveal the nature of the disturbance or the origin of the susceptibility."

W. A. PERLZWEIG

Chemical changes in the blood during immunization. G. L. ROHDENBURG, O. F. KREHBIEL, AND A. BERNHARD. *Am. J. Med. Sci.* 164, 361-79 (1922).—During the process of immunization with a definite antigen, disturbances in the N equil. and in the total solids occur, as well as changes in the blood-sugar and the pH values. Only the last two factors correlate with the antibody response.

G. H. S.

Physical chemistry of cancer. M. WATERMAN. *Z. Krebsforschung* 19, 101-4 (1922); cf. *C. A.* 17, 823.—This work is based on the observations of Clowes that tumor tissue is less resistant to elec. conduction than normal tissue. This is corroborated by W. It depends on the increased permeability of the cells to ions and the resistance can be restored exptl. *in vitro* by Ca ions. It is assumed that in the surfaces of the tumor cells there is an increased dispersion of the surface colloids, whereby the entrance of the dissolved ions is facilitated. W. suggests the possibility that the demonstration of a marked increase in resistance after addition of Ca may be used as an indica-

tion of malignancy of a tissue, not only *in vitro*, but possibly even in the living patient during operations. In experimental tar cancers in mice the electrochemical alterations may be demonstrated in the stage when the epithelium has shown itself to be of malignant character.

H. G. WELLS

Acidosis, alkalosis and tumor growth. W. H. WOGLOM. *J. Cancer Research* 7, 149-50(1922).—HCl of a strength from 0.1 to 0.2 *N* was given subcutaneously in the subcutaneous tissues of mice with transplanted tumors, and although the mice lost wt. the tumor growth was little if at all retarded. Enormous doses of NaHCO₃ caused, if anything, some increase in the tumor growth rate.

H. G. WELLS

Further studies on bacterial hypersusceptibility. II. HANS ZINSER AND JULIA T. PARKER. *J. Exptl. Med.* 37, 275-302(1923); cf. *C. A.* 16, 751.—When filtered alk. exts. of pulverized bacteria of several varieties are pptd. with acid in the cold, boiled with acid and all materials thrown down by these procedures removed, there remains a small amt. of an alc.-precipitable material which no longer gives any of the ordinary chem. reactions for proteins but is specifically precipitable by homologous antiseraums and gives sp. complement fixation reactions. Such material can also be obtained from organisms like the influenza bacillus, pneumococcus and meningococcus by extn. without preliminary grinding of the bacteria and is present in filtrates of young and old broth cultures of the organisms. These materials are believed to be analogous to tuberculin and to the pneumococcus substances of Dochez and Avery (*C. A.* 11, 3056). Boiling under a reflux at an acid reaction ranging from *p_H* 5 to 6 for 1 hr. failed to destroy the antigenic specificity of the residue antigen. The pneumococcus and tubercle bacillus residue antigens were resistant to both acid and alk. reaction after boiling 1 hr., but the alkali destroyed the staphylococcus and influenza residues. At an alk. reaction of *p_H* 9.4 the influenza residue deteriorated within 48 hrs., but the other antigens withstood such treatment for 6 days. Antibodies could not be produced in animals by injecting these residues.

C. J. WEST

Chloride retention in experimental hydronephrosis. N. M. KEITH AND D. S. PULFORD. *J. Exptl. Med.* 37, 175-86(1923).—In acute exptl. hydronephrosis Cl retention occurs as well as retention of H₂O, urea and phenolsulfonephthalein. If both H₂O and Cl are retained there may be no appreciable rise in the plasma Cl content. When Cl is retained, but not H₂O, the Cl content of the plasma rises strikingly. After the removal of the ureteral obstruction in acute hydronephrosis all renal functions, H₂O, Cl and urea excretion, may be rapidly restored in equal degree or the Cl may be retained temporarily while there is a free excretion of H₂O and urea. In chronic hydronephrosis adequate daily excretion of urea and Cl may be maintained by a compensatory polyuria. Cl retention or an abnormal Cl excretion may occur in certain renal lesions when there is no change in the urea, phenolsulfonephthalein or H₂O excretion. C. J. W.

Source of agglutinins in the milk of cows. THEOBALD SMITH, M. I. ORCUTT AND R. B. LITTLE. *J. Exptl. Med.* 37, 153-74(1923).—Expts. are reported which point to a distinct participation of the udder in the production of agglutinins when the gland is invaded by living or flooded by dead bacteria. The quarter injected reacts at first with a heavy influx of polynuclear leucocytes and later with an increase of agglutinins.

C. J. WEST

Endothelial reactions. VII. Changes in the distribution of colloidal carbon noted in the lungs of rabbits following splenectomy. NATHAN C. FOOT. *J. Exptl. Med.* 37, 139-51(1923).—After splenectomy in rabbits colloidal C introduced into the circulation is removed primarily by the lungs, which compensates for the loss of the spleen; they contain vastly more C than those of a normal rabbit. The cells phagocytosing colloidal G in the lung appear to be produced there, rather than in other organs, as proliferation of the endothelium occurs chiefly in the lung under these conditions. These cells either

remain in the pulmonary capillaries and lymphatics or are thrown into the circulation. In the latter case there is an apparent increase in the no. of macrophages in the lumina of the liver sinusoids, but nowhere else, indicating a transference of C from lung to liver within cells. C. J. WEST

LABBÉ, MARCEL: *Clinical Treatise on Diabetes Mellitus*. Translated, revised and edited by C. G. Custom. 382 pp. \$5. New York: William Wood & Co.

H—PHARMACOLOGY

ALFRED N. RICHARDS

The antipyretic action of dulcin. E. W. TASCHENBERG. *Deut. med. Wochschr.* 48, 695(1922).—Dulcin closely related to phenacetin in amts. greater than necessary to replace sugar has only an insignificant, if any, antipyretic effect. S. AMBERG

Treatment of cases of pharyngitis with Argaldon. SCHLESINGER. *Deut. med. Wochschr.* 48, 696(1922).—Argaldon is a combination of protein and $(CH_3)_6N_4$ from which alk. saliva liberates HCHO. Its use is recommended for gargling in 0.3-0.5% soln. S. AMBERG

The absorption of mercuric chloride and trypaflavine by bacteria and body cells. M. HAHN AND E. REMY. *Deut. med. Wochschr.* 48, 793-4(1922).—Guinea-pig liver and *B. coli* were used. The bacteria were grown 18 hrs. on agar. Weighed amts. of both were taken and furthermore the dry residue was detd. They were taken up and shaken in 1:1000 trypaflavine and 1:1000 $HgCl_2$ at 37°. Then the substances were detd. in the supernatant fluid obtained with the centrifuge. The bacteria removed much more trypaflavine and $HgCl_2$ than the liver. On transfusion of liver with trypaflavine in serum much less was taken up by the liver than when the trypaflavine was in Ringer soln. The same held true for $HgCl_2$. On the av. 100 g. moist coli substance took up 2.69 g. trypaflavine and 11.65 g. $HgCl_2$; 100 g. moist liver, 1.37 g. trypaflavine and 8.34 g. $HgCl_2$. S. AMBERG

Sennatin, a drug stimulating peristalsis. F. J. MEYER. *Deut. med. Wochschr.* 48, 1012-3(1922).—Sennatin is a fluid ext. prepd. from the active principles of senna leaves and can be injected intramuscularly with good effect on peristalsis. The dose is about 3 cc. S. AMBERG

The new trypanosome remedy "Bayer 205" and its significance for chemo-therapeutic research. M. MARTIN. *Deut. med. Wochschr.* 48, 1335-7(1922).—Nothing is known as yet about the nature of "Bayer 205" which has been used in the lab. and on patients for several years. Some results are given. It is easily sol. in water and can be given intravenously. In large doses, it is hemolytic, produces hemorrhages and nephritis in man. It is very effective in all trypanosome diseases hitherto investigated. S. AMBERG

Toxicity of aromatic nitro compounds. J. STUKOWSKI. *Deut. med. Wochschr.* 48, 1377-9(1922).—Description of cases of dinitrobenzene intoxications in workers with explosives. S. AMBERG

The action of novasurol on blood and diuresis. W. NONNENBRUCH. *Münch. med. Wochschr.* 68, 1282-3(1921).—Novasurol (a sol. Hg compound) is a very efficient diuretic, at the same time increasing the NaCl excretion, even on a salt-poor dry diet. NaCl of the blood serum and a number of red blood cells did not change definitely while the serum protein increased. The water loss is partially extrarenal. S. AMBERG

The limits of the chemotherapeutic activity of arsenobenzene derivatives on hog erysipelas, compared with the activity of hog erysipelas serum. W. KOLLE AND H. SCHLOSSBERGER. *Münch. med. Wochschr.* 68, 1439-41(1921).— $(3,4,5-(H_2N)_3C_6H_2AsO_2)_2$

and (4,3,5-MeHN(H₂N)₂C₆H₂As₂)₂ proved most efficient of the arsenobenzenes in their curative action on hog erysipelas in mice; they were effective when injected once every 24 hrs. after infection. Only antiserum has thus far been able to accomplish this result.

S. AMBERG

The diuretic activity of mercury studied with the organic mercury preparation novasurol. A. MÜHLING. *Münch. med. Wochschr.* 68, 1447-9(1922).—Novasurol is Na hydroxymercurichlorophenoxyacetate with diethylmalonylurea. It has a diuretic action, increasing the NaCl concn. of urine. The water diuresis is followed by a short increase of the refractometric value of blood serum, which soon changes to a decrease, that is diln. of blood serum. The concn. of uric acid and of creatinine are not influenced. Novasurol is recommended as a diuretic in cardiac edema.

S. AMBERG

The action of isopropyl alcohol on the functional force of the heart. RUSSEL BURTON-OPITZ. *Arch. néerland. physiol.* 7, 157-60(1922).—The physiol. action of EtOH and isopropyl alc. is compared by injecting into slightly narcotized cats and measuring the functional force of the heart by means of a "Strom uhr" inserted in the inferior vena cava. The aim of these expts. is the registering of the circulating current in the vena cava in relation to the arterial and the venous pressure, before and after a definite quantity of either of the 2 alcs. is injected. 3 cc. isopropyl alc. of 10, 25 or 50% did not considerably change the functional force of the heart; 3 cc. of 75 or 100% caused well defined vascular depressions; EtOH administered in the same concn. produced a similar depression but somewhat weaker. The results do not justify, however, the conclusion that EtOH is less toxic than isopropyl alc.

R. BEUTNER

The vaso-dilator action of adrenaline. E. WERTHEIMER. *Arch. néerland. physiol.* 7, 190-4(1922).—While moderate doses of adrenaline produce slight vasoconstriction, higher doses result in vasodilatation. These effects are observed by injecting adrenaline into the inner surface of the lips of a dog. The extensive literature on the subject is discussed in detail, but no decision can be reached on the basis of previous expts. as to the real point of attack of adrenaline.

R. BEUTNER

The influence of various alkaloids on the duration of gastric digestion of meat by the dog. EDGAR ZUNZ. *Arch. néerland. physiol.* 7, 276-80(1922).—A dog is injected with 5 or 6 mg. of various alkaloids per kg. of their weight. 20 or 30 min. after the injection 25 g. cooked meat per kg. are fed to the animal. After 9 or 10 hrs. the animal is killed and the content of the stomach is analyzed. In a normal animal, the digestion is completed during this time. The alkaloids injected retard the digestion; the total duration can be calcd. from the quantity of the undigested food found after 9 hrs. The following values are obtained: morphine meconate 25 hrs., morphine-HCl 24 hrs., thebaine-HCl 18 hrs., narcotine meconate 15 hrs., codeine-HCl 14 hrs., xanthaline-HCl 12 hrs., cryptopine-HCl 12 hrs., narceine-HCl 12 hrs., papaverine-HCl 10 hrs. A mixt. of 1 mg. codeine-HCl and 1 mg. morphine-HCl does not exhibit synergistic effects. The "narophine" recommended by Straub (*C. A.* 6, 2651) which is a double meconate of narcotine and of morphine increases the duration of the digestion to a degree as would be expected according to its compn. One or 2 mg. codeine does not change the normal duration of the digestion. 1/2 or 1 mg. atropine sulfate has the same action as 5 mg. narcotine meconate; atropine is, therefore, active in smaller doses than the other alkaloids investigated.

R. BEUTNER

The action of sulfurated mineral water on smooth muscles. ADRIANO VALENTI. *Arch. néerland. physiol.* 7, 496-501(1922).—Water from the spring S. Andrea di Bagni (0.16% H₂S) and from that of Tabiano (0.11% H₂S) caused contraction of isolated strips of guinea pig uterus or of frog stomach when added to the physiological salt solution in which they were suspended in the proportion of 1:6.

R. BEUTNER

Effects of exposure to arsenic trichloride upon the health. SHERIDAN DELÉPINE.

J. Ind. Hyg. **4**, 346-64(1922).—Guinea pigs, rats, rabbits, and mice were used. Undild. AsCl_3 applied to the skin causes necrosis in a short time. It is quickly absorbed and may be found in all tissues, especially in the brain, kidney and liver. When air contg. AsCl_3 in the ratio of 1 to 40,000 parts is breathed by mice for 5 min. death follows rapidly, with symptoms pointing to laryngeal obstruction. The extent of exposure to AsCl_3 may be ascertained by analysis of the hair, since the hair becomes impregnated very rapidly with the As.

A. A. CHRISTMAN

Colloidal chemistry and pharmacology. HANS HANDOVSKY. *Kolloid.-Z.* **31**, 287-9(1922).—A review. The action of drugs is dependent on the condition of the cell and its variation is distinctly due to a colloidal change. The pharmacologist ought not only to tell the physician what drug to use but how to use it.

A. A. C.

The treatment of pulmonary tuberculosis with sodium morrhuate. M. J. FINE. *Am. Rev. Tuberculosis* **6**, 934-7(1922).—In man results obtained with the usual form of treatment of pulmonary tuberculosis are as effective as, and probably more so than, those with Na morrhuate. It can at most only be considered an aid in the usual treatment of tuberculosis.

H. J. CORPER

The biochemical importance of organic mercury compounds. W. SCHÖELLER. *Naturwissenschaften* **10**, 1071-9(1922).—A review.

C. C. DAVIS

Alcohol and progeny. AGNES BLUM. *Z. ind. u. med. Hyg.* **28**, (1922); *Naturwissenschaften* **10**, 1058-9.—Not only the size, but also the no., of litters of mice was decreased by EtOH. EtOH caused an increase in sterile matings of normal mice from 16.24 to 61.97%. Mating of normal males with females treated with EtOH decreased the litter size from a normal of 4.94 to 3.85.

C. C. DAVIS

The action of protective colloids in colloidal metal solutions. RUDOLPH NISSEN. *Z. ges. exp. Med.* **28**, 193-233(1922).—Every intravenous injection of foreign protein or of colloidal metal solns. contg. such proteins produces a leucopenia of the peripheral blood followed by a leucocytosis. Repeated intravenous injection of electrocollargol results in a permanent leucocytosis (pseudoeosinophile) with all the signs of stimulation of the myeloblastic app. Repeated injections of electroferrol produces an additional stimulation of the erythroblastic app.

E. B. FINK

Hematologic studies in experimental collargol and arsphenamine intoxication. F. HERZOG AND A. ROSCHER. *Z. ges. exp. Med.* **28**, 224-45(1922).—Chronic intoxication with collargol in rabbits produces a progressive anemia without much change in the leucocytes. Chronic intoxication with neoarsphenamine produces no changes in the blood picture which can be called characteristic.

E. B. FINK

The influence of small quantities of methanol on nitrogen metabolism. KONRAD REWIGER. *Z. ges. exp. Med.* **28**, 368-77(1922).—A single non-toxic dose of CH_3OH (max. of 0.2 cc. per kg.) when fed to hungry dogs in N balance renders it negative. Amyl alc. has the same effect.

E. B. FINK

Pilocarpine and blood picture. H. ZUNTZ AND R. VOGEL. *Z. ges. exp. Med.* **29**, 159-68(1922).—The injection of pilocarpine into dogs in doses of 1.1 to 1.5 mg. per kg. body wt. leads to a leucocytosis which may reach 3 times the normal count. The polynuclears are increased both relatively and absolutely. The lymphocytes, mononuclears and transitional cells are not characteristic in their behavior. The eosinophiles practically disappear in 4 to 5 hrs. The hemoglobin rises with concn. of the blood through loss of fluid but does not keep pace with the leucocytosis. Splenectomy has no influence upon the leucocytosis produced by pilocarpine. Pilocarpine and atropine are antagonists with respect to their action in producing leucocytosis.

E. B. FINK

Quinidine in auricular fibrillation, with some observations on its use in combination with digitalis. T. S. HART. *Arch. Intern. Med.* **30**, 593-605(1922).—"Quinidine

administered in 15 cases of auricular fibrillation was followed by sinus rhythm 10 times in 5 cases. In 2 paroxysmal cases it was followed by sinus rhythm in both cases. Cases exhibiting electrocardiograms with coarse auricular waves appear to be more readily affected by quinidine. Quinidine decreases the auricular rate and augments the ventricular rate. Digitalis increases the auricular rate and slows the ventricular rate. A case of paroxysmal auricular fibrillation is reported in which under the daily administration of quinidine no paroxysms have occurred for 8 months." I. GREENWALD

The effect of the administration of hypertonic salt solution on the blood volume and certain related blood constituents. A. L. BARACH, Wm. MASON AND B. P. JONES. *Arch. Intern. Med.* 30, 668-87(1922).—Six patients with brain tumor and one with a fractured skull received 100 cc. 15% NaCl intravenously.—The plasma vol. was increased by between 15 and 30% of the original blood vol., or 500 to 1200 cc. (calcd.). The observed increases in the 2 cases in which the vital red method was used were 761 and 894 cc., resp. The blood vol. returned to the original vol. within 3.5 hrs., except in one case with an abnormally low blood vol., in which the increase persisted for 4 days. Oral administration to a patient with polycythemia and to a normal person and to rabbits had similar, but less marked, effects. No ill effects were observed, either clinically or by detns. of O₂ satn., CO₂ content, free hemoglobin or bile pigment in the serum etc., but in the one patient who received hypertonic Ringer soln., the serum showed signs of hemolysis. In the 6 patients with brain tumor, who had an increased cerebrospinal pressure, symptomatic improvement (relief of headache and stupor) occurred in all.

I. GREENWALD

The effect of atropine on gastric function, as measured by fractional analysis. B. C. LOCKWOOD AND H. G. CHAMBERLIN. *Arch. Intern. Med.* 30, 806-16(1922).—The administration of 0.02 grain of atropine, by mouth or subcutaneously, depressed both the free and total gastric acidity about 30% (cc. 0.1 N acid per 100 cc. of fluid), delayed the evacuation time after an Ewald meal about 10 min. and brought about a more frequent appearance of bile in the gastric contents.

I. GREENWALD

Studies in the chemotherapy of bacterial infections. II. The chemotherapy of experimental localized bacterial infections with special reference to pleuritis. J. A. KOLMER. *Arch. Intern. Med.* 31, 9-14(1923); cf. *C. A.* 16, 4282; 17, 819.—The amt. of a drug required to be injected intravenously, intraperitoneally or subcutaneously in order to preserve the lives of a significant number of animals is often very nearly as great as the lethal dose. But, if the infection be localized in certain serous cavities and if the injections be made into these same cavities, the ratio of the tolerated dose to the sterilizing dose is much greater and chemotherapeutic studies can more readily be made. It is recommended that the test animal should have some natural immunity towards the test organism in the desired location, as the guinea pig for pneumococcus pleuritis, and pericarditis, the rat or dog for pneumococcus meningitis and the dog or rat for tuberculous pleuritis. The organism should be of moderate, not extreme, virulence, in order to reduce the likelihood of extensive invasion of the blood or other organs.

I. GREENWALD

An experimental and clinical study of quinidine sulfate. I. Experimental. H. M. KORN. *Arch. Intern. Med.* 31, 15-35(1923).—Administration of quinidine sulfate by vein to dogs or by mouth to guinea pigs may temporarily accelerate, but ultimately retards, the rate of impulse discharge from the pacemaker. In the dog, but not in the guinea pig, there is depression of intra-auricular conduction, leading to partial or complete intra-auricular block, which is abolished by vagus stimulation. There is depression of auricular-ventricular conduction, which, in the late stages of poisoning in the guinea pig, may lead to a 2:1 response in the ventricle, but not to a greater. There is delay in ventricular conduction. Death occurs, in dogs, from ventricular

fibrillation; in guinea pigs, by gradual inhibition of the whole heart. Intra-auricular block in a patient, after administration of quinidine, is reported. II. Clinical. *Ibid* 31, 36-55(1923).—Report of experience with quinidine in 36 patients, of whom 32 received a full course of treatment and 20 of these responded with normal mechanism. Not all could be carefully followed but at least 15 secured permanent benefit. "Quinidine is universally a heart muscle poison. In each patient an estimate of this effect must be carefully weighed against the expectation of benefit to be derived from restoration of normal sinus mechanism."

I. GREENWALD

The action of alcohols on the heart in relation to their chemical constitution. P. WOLFF. *Biochem. Z.* 132, 480-4(1922).—Action on the isolated frog heart of various cardiac toxins is not influenced by weak concns. of MeOH, EtOH or iso-PrOH. The validity of Richardson's law for the 3 alcs. was confirmed for the heart of cold-blooded animals. The effect of these compds. is reversible. The 2 higher show a significant excitatory action after the depression which is not exhibited with MeOH. The state of contraction with MeOH is diastolic and tends towards the systolic with the higher homologs.

F. S. HAMMETT

The role of acid in adrenaline hyperglucemia. F. KORNFIELD AND H. ELIAS. *Biochem. Z.* 133, 192-211(1922).—Subcutaneous injections of adrenaline in rabbits induce hypocalcemia of some hrs. duration. This phenomenon is not produced in dogs. When man is similarly treated there occurs only a minor lowering of the CO₂ tension of the alveolar air of short duration. The reaction may even not occur at all. Hypocalcemia, therefore, is not an essential preliminary for adrenaline hyperglucemia. The question as to whether a local acidification of the liver is of significance in adrenaline hyperglucemia was not answered by these studies.

F. S. HAMMETT

The action of quinine and atoxyl on pancreatic lipase. P. RONA AND R. PAVLOVIC. *Biochem. Z.* 134, 108-17(1922); cf. *C. A.* 16, 2871.—Pancreatic lipase from H₂O ext. of human pancreas and pancreatic fistulas in dogs is markedly slowed in its action by quinine-HCl. The logs of the quinine concn. form a straight line when plotted against the logs of the inhibitory action. The poisoning effect increases with time and is not reversible. Pancreatic lipase is not poisoned by atoxyl while liver lipase is extraordinarily sensitive. NaF inhibits the activity of pancreatic lipase but little, while it retards the activity of liver and serum lipase greatly.

F. S. HAMMETT

The action of quinine and its derivatives on gastric lipase. P. RONA AND M. TAKATA. *Biochem. Z.* 134, 118-30(1922).—Gastric lipase obtained from the Pavlov stomach of a dog is retarded in its activity by quinine. The extent of the retardation is dependent upon the H-ion concn. of the soln. (representing the degree of dissociation of the quinine) and on the concn. of the quinine, but not on the concn. of the enzyme. The quinine-retardation curve is that of an adsorption isotherm. The poisoning is reversible. The action of vucine is similar. The quinine derivs., quinidine, optochin, cucupine, and vucine, exert a retarding influence on gastric lipase according to their ability to lower surface tension.

F. S. HAMMETT

Pharmacology of selenium and tellurium. IV. Action of their acids on trypanosomes in vitro. F. LEHMANN. *Biochem. Z.* 134, 390-7(1922).—Trypanosomes die within the hr. when kept in NaCl and Ringer soln.; when kept in Tyrode soln. and dil. bouillon they live for several hrs. The organism is killed by high concns. of Se and Te. The following concns. are apparently harmless when in contact with the organisms for 1 hr.: Na₂TeO₃, 1:500; Na₂TeO₄, 1:300; Na₂SeO₃, 1:500; Na₂SeO₄, 1:100. No decrease in reproductive velocity (virulency) follows treatment with Se and Te. Selenites and tellurites are more toxic than selenates and tellurates.

F. S. HAMMETT

Oligodynamic action of metals. J. SCHUMACHER. *Biochem. Z.* 134, 398-404(1922).—The presence of free metallic ions in oligodynamic H₂O can be demonstrated

by leuco-methylene blue. These free ions act catalytically as O carriers. Complex ions do not act this way. The O carrier activity of the metals can be shown histochemically after the combination with the dead cells is accomplished. The oxidation processes of the living cell are also increased by the free metal ions when present in small amts. as shown by increased metabolism and growth. F. S. HAMMETT

The transference of ethyl alcohol from mother to fetus. J. OLOW. *Biochem. Z.* 134, 407-14(1922).—When pregnant women are given EtOH just before delivery it is distributed throughout the maternal body and also that of the child. It can be detected in fetal blood within 12 min. after ingestion. The diffusion is not instantaneous, for it is not until 40 min. after ingestion that equal concns. are found in maternal and fetal blood. Many factors obviously are concerned under the conditions in force at the time. The decrease in the EtOH concn. of the maternal blood runs approx. parallel to that of the fetal. F. S. HAMMETT

Neo-antilueticin (Antimonhydrargyrum) M. TSUZUKI. *Deut. med. Wochschr.* 48, 1511-2(1922).—Neo-antilueticin (NA), $[SbO(C_4H_4O_6)]_3K \cdot NH_4 \cdot C_2H_5O_8SNa \cdot Hg_2 \cdot 2H_2O$, is a double salt of K NH_4 antimonytartrate and the neutral Na sulfonate of mercurized salicylic acid. The cryst. powder dissolves rapidly in water to give a neutral soln., but is insol. in alc. and ether. It decomposes when heated in H_2O soln! above 60° . The aq. soln. gives a ppt. with $Ca(OH)_2$ (Ca tartrate) and a violet coloration with $FeCl_3$. Both Sb and Hg are pptd. as sulfide when the acidified (HCl) soln. is treated with H_2S . Hg is not present in a highly ionized condition because KI, NaOH, and yellow $(NH_4)_2S$ in excess do not call forth a ppt. $(NH_4)_2S$ ppts. Sb_2S_3 at first, but this redissolves in an excess of the reagent. The compd. is recommended as a substitute for salvarsan in syphilis. MILTON HANKE

Narcosis and acidosis. P. GYÖRGY AND H. VOLLMER. *Klin. Wochschr.* 1, 2317-8 (1922).—Narcosis with $CHCl_3$ and Et_2O markedly reduces the metabolism rate and leads to a systemic acidosis. The urine excreted immediately after the narcosis is dark colored and highly concd. A comparison of this urine with that collected before the narcosis shows that the anesthesia has markedly increased the excretion of total N, NH_3 , NaH_2PO_4 and acid. The p_H of the urine is reduced. MILTON HANKE

Modern treatment of leprosy with chaulmoogra derivatives. OLFF. *Klin. Wochschr.* 1, 2336-8(1922).—A review with what appears to be a good bibliography. MILTON HANKE

Hemolysis with mercury and mercury compounds. H. BECHHOLD. *Arb. Staats-inst. Exptl. Therap.* 1920, No. 2, 27-48.—The irreversible coagulation of red blood by $HgCl_2$ cells goes parallel with the irreversible pptn. of hemoglobin. If the concn. of $HgCl_2$ is too low to ppt. the hemoglobin or serum, hemolysis is produced. The coagulation of blood cells and hemoglobin is the result of the action of the Hg ion, and is obtained only with ionizable Hg compds. The coagulation with different Hg compds. is proportional to the ionization of the compds. If the ionization of $HgCl_2$ is lowered by the addition of NaCl, which also increases the concn. of $HgCl_2$ mols., the zone of coagulation is decreased. The hemolysis is the result of the $HgCl_2$ mol. Metallic Hg and HgO , in powder or colloidal form, are hemolytic. Since Hg is insol. in H_2O but slightly sol. in lipoids, the latter in the red cells is responsible for the hemolysis. In coagulation of red cells by $HgCl_2$, the latter is bound. With identical amts. of red cells the coagulation is proportional to the abs. quantity of $HgCl_2$ and not the concn. The presence of proteins, cholesterol and lecithin in the medium inhibits coagulation and hemolysis. The limit of the hemolytic action on red cells, on the toxic action for frogs and on the sense of taste lies at about the same level. Since $HgCl_2$ at this level has no action on proteins these 3 different actions take place through the medium of lipoids. In warm-blooded animals (white mice) the acute toxic action of $HgCl_2$ increases with the

increase of the hemolytic component of HgCl_2 (addition of NaCl). The toxic action of HgCl_2 then, is not due to the coagulation of proteins but to that action which is dependent on lipoids.

JULIAN H. LEWIS

Nontoxicity and antipyretic efficiency of tolysin (ethyl ester of *p*-methylphenyl-cinchonic acid). H. G. BARBOUR AND E. LOZINSKY. *J. Lab. Clin. Med.* 8, 217-26 (1923).—Tolysin, administered *per os*, even up to doses of 50 g. per kg., or 5% of the animal's own wt., produces no effect upon the general condition of the dog. Tolysin seems to be the least toxic of all substances of demonstrated antirheumatic efficiency. It exhibits a peculiarity in pharmacol. behavior in that the max. limit of absorption from the intestine coincides essentially with therapeutic doses. As cumulation is entirely absent, indefinitely large amts. are non-toxic, at least for dogs.

E. R. LONG

Report of a case of chronic hydrocyanic acid poisoning. JACOB ROSENBLUM. *J. Lab. Clin. Med.* 8, 258-9 (1923).—A chemist, who had worked for 9 mos. on a problem in which much HCN was used, suffered in the last month from loss of energy, vomiting and twitching of the eyes. A moderate secondary anemia was found.

E. R. LONG

Physiological study of the phenomena of shock: nitritoid crisis produced by intravenous injection of arsenobenzene. MARCEL POMARET. *Lancet* (French Supplement) 1922, II, 1178.—Arsenobenzene in aq., non-alkalized soln. ppts. proteins in consequence of the presence of phenolic groups in the mol. The "nitritoid crisis" observed on the injection of arsenobenzenes into dogs is the result of the intravascular flocculation consequent upon the formation of the arsenobenzene-protein adsorption complex. The symptoms are the same as those in phenolic shock induced by phenol and trinitrophenol. The As of the mol. is not concerned. The surest way of avoiding nitritoid crisis is by administering As compds. intramuscularly.

E. R. LONG

Variations of blood pressure under intravenous injection of phenolic compounds (arsenobenzenes, 606, 914, etc.). M. POMARET. *Lancet* 1922, II, 1220-1; cf. preceding abstr.—The fall of blood pressure and other symptoms of shock following intravenous injection of arsenobenzenes are phenolic shock symptoms resembling the shock symptoms registered after intravenous injection of simpler phenol compds. as trinitrophenol and phenol. The shock is the more profound the more acid the soln. is and the greater, accordingly, its pptg. power for proteins.

E. R. LONG

The anti-coagulating properties of the arsenobenzenes. CH. FLANDIN AND A. TZANCK. *Lancet* (French Supplement) 1922, II, 1177-8.—The arsenobenzenes have an anticoagulating action *in vivo* and *in vitro*. Blood collected in a clean glass receptacle, the sides of which have been moistened with a weak arsenobenzene soln., will remain uncoagulated indefinitely. In blood taken from an individual who has received an intravenous injection of arsenobenzene clotting is delayed 30 min. to 24 hrs. The anti-coagulating effect is due absolutely to the arsenobenzene, not the syphilis. Advantage may be taken of the property in blood transfusion and blood letting.

E. R. LONG

The treatment of syphilis by intramuscular injections of aminoarsenophenol (Pomaret 132). MARCEL BLOCH. *Lancet* 1922, II, 1179-80.—Aminoarsenophenol can be given by intramuscular injection in such quantities that treatment of syphilis may be pushed vigorously, while at the same time the phenomena of shock are avoided. Rapid absorption of the medicament occurs. Larger doses are possible than can be tolerated by intravenous injection.

E. R. LONG

Emetine bismuthous iodide in the treatment of amebiasis. P. M. RENNIE. *Lancet* 1922, II, 1374-6.—Administered in 1-3 courses of 12-45 grains each this compd. had a definite curative action on amebiasis.

E. R. LONG

The pharmacology of sodium citrate. II. The influence of sodium citrate on peristalsis. W. SALANT, N. KLEITMAN AND L. H. WRIGHT. *Am. J. Physiol.* 62,

531-41(1922); cf. *C. A.* 16, 3710.—Sodium citrate intravenously or intramuscularly stimulated the motor functions of the intestines, the action on the small intestine being greater than on the larger. The action varied in different animals. Stimulation of tonus predominated in dog's intestines. Augmentation of the rhythmic contractions was largely observed in the rabbit while both occurred in cats. With the isolated intestine the main effect of sodium citrate was stimulation in rabbit's intestine, and depression in cat's intestine. There is evidence that the stimulation of the intestine in intact animals by sodium citrate is due to its action on the motor nerve fibers and not on the muscle substance. Depression in isolated intestine may be due to stimulation of the inhibitory mechanism.

J. F. LYMAN

On the mode of elimination of minute quantities of salicylate through the urine.

H. HERISSEY, N. FIESSINGER AND J. DEBRAY. *Compt. rend. soc. biol.* 87, 625-6(1922).—Urine gives a positive reaction even when 2 mg. of Na salicylate is administered by mouth. When 0.2 g. are given, the positive reaction lasts until 6 hrs. later. It is not believed that the liver retains the salicylate and the fact that in cases of cirrhosis the reaction is not so well marked is attributed to purely mech. conditions resulting from portal stasis.

S. MORGULIS

Rise of sugar level in blood and cerebrospinal fluid under the influence of adrenaline. M. POLONOVSKI, E. DUHOT AND MOREL. *Compt. rend. soc. biol.* 87, 679-80 (1922).—Hyperglycemia produced exptly. is accompanied by a rise in the sugar content of the cerebrospinal fluid. This fact is emphasized as a precaution in the utilization of the cerebrospinal fluid for diagnostic purposes since its sugar level will be affected by any factor which will cause a rise in blood sugar.

S. MORGULIS

Effect of adrenaline on the striated muscle system. J. GUGLIELMETTI. *Compt. rend. soc. biol.* 87, 692-4(1922).—Adrenaline has little influence on the excitability of either the muscle or the nerve of a complex neuromuscular mechanism which is not fatigued. It restores the original excitability to a fatigued muscle whose chronaxie has been increased, but is unable to affect the excitability of a denervated muscle whether fatigued or not. Furthermore, adrenaline is without influence on a curarized muscle, and the results are the same with fatigued and non-fatigued muscles. G. destroyed the splanchnics and tested the effect of adrenaline one month after the operation in the surviving animals. There was no difference in the behavior between these and normal animals. Adrenaline acts upon some substance which according to Langley and Lucas is found at the juncture between muscle and nerve.

S. MORGULIS

The toxic action of toad venom on man and animals. VINCENT NOVARO. *Compt. rend. soc. biol.* 87, 824-6(1922).—Attaching toads to the skin of dogs, especially if the hair was shaved off, and leaving them there for 1 hr. (secretion was provoked either by elec. stimulation or with ether) caused death in about an hr. The animal showed marked bradycardia, intense mydriasis, an advancing paralysis, etc. Analyses of the secretion from different toads (squeezed from the parotids) gave 34-38% of dry substance and 1-3% of adrenaline in the fresh secretion. The mortal dose, per kg., was as follows for different animals: pigeon 1 mg.; rabbit 0.5-5 mg. intravenously or 30 mg. subcutaneously (ingestion of 500 mg. was without effect); 2.5 mg. guinea pig intravenously or 100 mg. subcutaneously and 25 mg. intraperitoneally; frogs 100 mg. subcutaneously; rats 250-350 mg. subcutaneously or intraperitoneally; toads unaffected by 500 mg.

S. MORGULIS

A study of the toxicity of the vapors of certain chemical substances on Phlebotomes. E. PRINGAULT. *Compt. rend. soc. biol.* 87, 846-8(1922).—The efficiency of vapors of SO_2 , HCN, MeOH, EtOH, HCHO, Et₂O, CHCl_3 , pyridine, nicotine and cresols has been tested. Only the cresols have proved of actual value, the alc., aldehydes, hydrocarbons, and Cl derivs. of the fatty acid series requiring very large doses.

S. MORGULIS

Toxicity of an arsenical glucoside: glucoside-dihydroxydiaminoarsenobenzene. A. LUQUER. *Compt. rend. soc. biol.* **87**, 1020-2(1922).—Experimenting with the compound produced by adding 2 glucose mols. to arsephenamine it was found that its toxicity for rabbits is only about $\frac{1}{2}$ as great as with arsephenamine. With the former the lethal dose was 0.6 g. per kg. of body wt. while with the latter 0.35 g. per kg. was invariably fatal. The comparison of the toxicity was made on the basis of the same content of As. S. MORGULIS

Quantitative data on levo- and dextro-adrenaline and on adrenalone. L. LAUNOV AND B. MENGUY. *Compt. rend. soc. biol.* **87**, 1066-8(1922).—The toxicity of the levo-adrenalines, natural and synthetic, is the same (of the same rotating power); that of the dextro is 20 times less and of adrenalone 100 less. From the point of view of the effect on the cardio-vascular system, the substances were studied in such doses, as to produce a min. hypertension, medium and max. possible hypertension. These 3 effects could be elicited with the levo-adrenalines (natural or synthetic) in doses of 1:5:15 to 1000000 per kg. of wt. (rabbit), resp.; with the dextro-adrenaline—50:150:1000 to 1000000; and with the adrenalone—500:1500:5000 to 1000000. S. MORGULIS

The mechanism of cardiac acceleration through quinine and other alkaloids of the cinchona bases. A. CLERC AND C. PIZZI. *Compt. rend. soc. biol.* **87**, 1075-7(1922).—Quinine which exercises a depressing action on the myocardial fibers causes a certain acceleration of the heart in small doses. The object was to det. whether this effect of the small doses is due to its paralysing action on the vagus center, the acceleration following then indirectly from the abolition of the antagonism to the sympathetic. The cardiac activity of dogs under chloral anesthesia was examd. with the string galvanometer in a state of repose and after an intravenous injection of quinine-HCl. 0.01 g. per kg. was sufficient to abolish the oculo-cardiac reflex, which is about the amt. necessary to offset the action of adrenaline. When only 0.005 g. was used the acceleration was produced but the oculo-cardiac reflex still persisted, so that the possibility of a paralysis of the vagus center was thereby excluded, the effect being due apparently to a direct stimulation of the accelerator fibers. The same results could be gotten with quinidine, cinchonine, and cinchonidine. S. MORGULIS

Aluminium potassium nitrate in the treatment of suppurative conditions, particularly osteomyelitis. MAX THOREK. *Ann. Surg.* **77**, 38-47(1923).—One g. mol. $\text{Al}(\text{NO}_3)_3$ and 3 g. mols. KNO_3 were crystd. from concd. HNO_3 . The rhombic and monoclinic crystals obtained have the compn. $\text{AlNO}_3 \cdot 3\text{KNO}_3 \cdot 10\text{H}_2\text{O}$ and are easily sol. For use one part of the double salt soln. is dild. with 9 parts of KNO_3 soln. and incorporated into the dressings. The double salt is not an antiseptic but is a definite accelerator of bacterial growth, "tending by rapid propagation to lower the vitality of the infective organisms, thereby assisting the normal resisting powers of the body to eliminate the invading organisms. The compd. does not attack normal tissues and does not interfere with granulation and normal osteogenic processes." Protocols of some successfully treated cases are given. W. A. PERLZWEIG

Antimony and sulfur in the treatment of lepers. F. G. CAWSTON. *J. Trop. Med. Hyg.* **25**, 345-6(1922); cf. C. A. **15**, 1160; **17**, 433.—Further reports on the use of some com. colloidal preps. of Sb in leprosy. W. A. PERLZWEIG

Induced spontaneous transformation of the cardiac depressant action of saccharin into cardiac stimulation. M. HEITLER. *Wiener klin. Wochschr.* **35**, 935-7(1922); cf. C. A. **16**, 1283.—Saccharin is a heart depressant, and its addn. to stimulating substances may abolish the action of the latter. Saccharin warmed or rubbed alone or with other substances (foods) or subjected to elec. current becomes a heart stimulant, the stimulating effect being temporary in character. On the other hand saccharin mixed and warmed with NH_4Cl or with $(\text{NH}_4)_2\text{CO}_3$ becomes a more intense and a more perma-

nent stimulant. Ordinary saccharin on prolonged standing spontaneously loses much of its sweetness, develops an unpleasant bitterish taste and becomes a stimulant. The NH_4 salt mixts. of saccharin retain their sweetness for long periods and their heart stimulating action does not change readily on standing. W. A. PERLZWEIG

Action of several groups of local anesthetics as determined by different methods. KONRAD FROMMERZ. *Arch. expl. Path. Pharm.* 93, 34-91(1922).—The toxic effect and the power to induce local anesthesia of a large series of compd. were detd., employing the rabbit cornea and the frog nerve-muscle prepn. An essential factor governing the effect produced is the concn. in which the substance reaches the point of attack, and this in turn is detd. by chem. and phys. properties. The degree and ease with which a compd. is decompd. and the readiness with which it is absorbed and diffused are fundamental. Thus, the action of a compd. upon nerve endings may not correlate in any way with the effect of the substance when, by infiltration methods, it is allowed to act upon the nerve-trunk. The differences in the anesthesia induced in a mucous membrane by diff. anesthetics are detd., both as to intensity and duration, not so much by a failure in absorptive processes as by the fact that with certain compds., as novocaine, diffusion is much more rapid than with others, as cocaine. Among the substances tested were complex carbonic acid esters, aromatic alic., novocaine and cocaine, eucupine and vucine, and the ethyl benzoyl- α -diethylaminoethyl- β -hydroxybutyrate. G. H. SMITH

Non-specific stimulus therapy. III. H. FREUND AND R. GOTTLIEB. *Arch. expl. Path. Pharm.* 93, 92-114(1922); cf. *C. A.* 16, 3333.—The injection of non-sp. proteins, such as heterologous serum or caseosan, or the simple process of bleeding, results in the development of a type of allergy or hypersensitiveness to unrelated, but physiologically active, substances, such as adrenaline and pilocarpine. This altered reactivity, manifested by a response to the injection of what normally was a non-reactive quantity of the drug, persists for a considerable length of time. The extent of the reactions was detd. with adrenaline by blood pressure changes; with pilocarpine by changes in salivary secretion. IV. Atropine-like action of human serum. H. STRUCK. *Ibid* 140-49.—There are substances in pathol. sera, particularly in infectious diseases and in carcinoma, and also in the serum during pregnancy, which exert an atropine-like action upon the frog heart which has been rendered inactive by muscarine. These substances are to be found in the fraction of serum which is sol. in alc. The serum of normal individuals, or alc. exts. of such sera, fail to activate a subreactive dose of atropine. G. H. SMITH

Physiology and colloid chemistry of the mechanism of the contraction induced in striated muscle by poisons. III. Caffeine contraction. OTTO RIESSER AND S. M. NEUSCHLOSZ. *Arch. expl. Path. Pharm.* 93, 163-78(1922); cf. *C. A.* 16, 2929.—The contraction of striated muscle induced spontaneously by large doses of caffeine or by smaller doses in conjunction with elec. stimulation is associated with a marked loss of the muscle in lactacidogen phosphoric acid. After recovery of the muscle a normal value for this substance is never restored. The most significant action of caffeine consists, therefore, in an interference with this restitution process. After an intense intoxication and increase in lactacidogen decompn. takes place and this leads to an acid accumulation in the muscle with a resultant acid contraction. Aside from the reversible nature of the early stages of caffeine contraction the condition resembles heat rigor or rigor mortis. H_2PO_4 elimination is increased in the muscle poisoned with caffeine. The metabolic changes induced by caffeine are apparently dependent upon alterations of a phys. nature which the caffeine brings about in the muscle colloids. IV. Veratrine action. *Ibid* 179-207.—Veratrine does not cause, either in high or low concns., any change in the lactacidogen component of the muscle. A marked effect is, however, induced in the H_2PO_4 elimination, since in low concns. the veratrine leads to diminished, in high concns.

to increased, excretion. High concns. of veratrine also prevent the paralysis caused by sugar solns.

G. H. SMITH

Effect of atropine and pilocarpine upon antibody production in rabbits. GEORG JOACHIMOGLU AND Y. WADA. *Arch. expl. Path. Pharm.* 93, 269-84(1922).—Rabbits injected with typhoid bacilli also received injections of atropine or pilocarpine and the antibody response (agglutinins) was detd. In general, the concn. of agglutinins in the sera was lower than that in control rabbits which did not receive the drugs. G. H. S.

Mode of action of tetrodotoxin (Fugu toxin). K. IWAKAWA AND S. KIMURA. *Arch. expl. Path. Pharm.* 93, 305-31(1922).—The pharmacol. action of an aq. ext. of the roe of the Japanese Fugu was detd. The toxin acts upon the medullary centers, causing paralysis of respiration and a fall in blood pressure. The effects differ in diff. animal species and vary with the mode of application. In the frog the brain is first affected, later the spinal cord. Upon the motor nerves it reacts like curare, and upon sensory nerves it acts as an anesthetic, like cocaine. Through a central action it causes a constriction of the frog pupil. In warm-blooded animals the motor paralysis first affects the phrenic nerve, and the character of the action depends upon the amt. of toxin absorbed. The toxin has an antipyretic action. Respiratory activity is stopped by the intravenous injection of weak solns., 0.014 to 0.017%; higher concns., 5%, are effective when administered subcutaneously. Adrenaline exerts a definitely antagonistic action to the toxin, as does pituitrin also.

G. H. SMITH

Combined action of ions and organic poisons. II. HANS HANDOVSKY. *Arch. ges. Physiol.* (Pflüger's) 195, 253-65(1922); cf. C. A. 16, 2930.—The effect of various ions upon saponin hemolysis of erythrocytes was detd., the results showing that all Mg salts intensify the action, $MgSO_4$ being more active than $Mg(SCN)_2$. In sugar-erythrocyte mixts. the sugar and Mg are antagonistic. With Ca hemolysis the degree of lysis is proportional to the Ca concn., being independent of the sugar. In the saponin hemolysis of blood the recognized biol. and chem. antagonisms between mono- and bivalent ions holds.

G. H. SMITH

Oligodynamic toxic action of metals on living substance. I. Paramécia. I. LÖHNER AND B. E. MARKOVITS. *Arch. ges. Physiol.* (Pflüger's) 195, 417-32(1922).—When tested upon paramécia the oligodynamic action of Cu manifests itself in 2 stages: a stage of excitation evidenced by increased locomotion, and a stage of paralysis characterized by loss of motility and by morphological changes. It is evident that the oligodynamic toxic action of metals is to be correlated with the degree of absorption of the metal by the living substance.

G. H. SMITH

Removal of heart intoxication by calcium and other bivalent cations. ERNST WIECHMANN. *Arch. ges. Physiol.* (Pflüger's) 195, 588-601(1922).—The paralysis of the heart induced by quinine or As may be overcome by Ca or by Sr and Ba but other ions are without effect. A similar antagonistic effect is exerted toward quinidine. Digitalis and strophanthin both act upon the heart stopped by quinidine to restore its action. The actions of K, As, and quinine upon the heart are not the same, since the effect of K can be neutralized by Ca, Sr, Ba, Co, Mn, and Ni, while that resulting from quinine or As is neutralized only by Ca, Sr, and Ba.

G. H. SMITH

Quantitative activity of homologous quaternary ammonium bases. FRITZ KÜLZ. *Arch. ges. Physiol.* (Pflüger's) 195, 623-5(1922).—Reacting upon nerve-muscle prepus. the following compds. were effective in the concns. indicated: NMe_4I N/5000-6000, NMe_4EtI 0.0005 N, NMe_4PrI N/700, NMe_4BuI N/8000, NMe_4AmI 0.0001 N, $NMe_4C_6H_{13}I$ 0.0001 N, $NMe_4C_8H_{17}I$ N/10,000-12,000, NEt_4MeI N/200-300, NEt_4I N/200-300, NEt_4PrI 0.002 N, NEt_4BuI 0.0005 N, NEt_4AmI N/4000, $NEt_4C_6H_{13}I$ N/15,000.

G. H. SMITH

Chemical and pharmacological aspects of unsaturated radicals. III. J. v. BRAUN

and GEORG LEMKE. *Ber.* 55B, 3536-59(1922).—A continuation of *C. A.* 12, 2197; 14, 3081, to det. whether (1) the particular physiol. activity of compds. with allyl groups, (2) the loose linkage of the allyls to O, N, S, and halogen, and (3) the β , γ -position in the allyl group, constitute 3 interdependent factors. The double bond in the β , γ position was found to cause the loose linkage, as shown by the similar physiol. behavior of *N*-allylnorcodeine and *N*-cinnamylnorcodeine. The radical $\text{CH}_2\text{CH}:\text{CHCH}_3$, present in butadiene dibromide, $(\text{BrCH}_2\text{CH})_2$, may be considered as a double allyl group, and is capable of giving cis and trans isomers. Because of the instability of the liquid (cis) isomer of butadiene dibromide, v. B. and L. were confined to the use of the stable trans isomer. Comparisons were made of the compds. $(\text{RCH}_2\text{CH})_2$ (A) and $(\text{RCH}_2\text{CH}_2)_2$ (B), where R was Br, PhO, SCN, and Me_2N . The bromide of A hydrolyzes much more easily than that of B; addition of Me_2N and reaction with RMgX are also much easier with A. In general, the butadiene and the allyl groups are similar in the loose linkages to halogen, O, N, and S. Ring formation with $\text{CH}_2\text{CH}:\text{CHCH}_2$ is more difficult than with the satd. chain. A number of compds. were prepd. with the butadiene chain, and compared in physiologic action with the corresponding allyl compds. The butadiene radical causes great diminution of physiol. action, although the chem. nature of the two series is very similar. This is due either to the large increase in size of the radical, or to the fact that the physiol. active nucleus of the mol. is distorted and rendered inactive.

E. H. VOLWILER

The mechanism of the vomiting induced by tartar emetic. SOMA WEISS AND R. A. HATCHER. *J. Exptl. Med.* 37, 97-111(1923).—It seems probable that the path taken by afferent emetic impulses induced in the gastrointestinal tract by tartar emetic depends upon the innervation of the organ concerned and not on any selective action of the poison on the afferent nerve.

C. J. WEST

Cumulative action of cobra venom. A. R. CUSHNY. *J. Pharmacol.* 20, 233-46 (1922).—Cobra venom, injected intravenously, is cumulative in action in rabbits inasmuch as small doses, even $\frac{1}{8}$ of the minimal lethal dose, given repeatedly prove fatal. This appears to be due to the slow inactivation or elimination of the poison which seems to vary somewhat in different individuals. A small part of the venom injected is eliminated or inactivated and this seems to occur soon after the injection, while later the quantity in the tissues is reduced only gradually. This may perhaps arise from the combination with the tissues occurring only slowly, and thus a certain amt. of venom escaping before it is anchored.

C. J. WEST

Action of barium. WM. SALANT AND NATHANIEL KLEITMAN. *J. Pharmacol.* 20, 247-63(1922).—The action of Ba varies with the condition of the organs with which it comes in contact. The action on different animals and in connection with different drugs is discussed.

C. J. WEST

Effect of epinephrine on excised strips of frog digestive tracts. C. M. GRUBER. *J. Pharmacol.* 20, 321-57(1922).—No difference was observed in the activity of the digestive systems of recently caught and starved frogs. The longitudinal muscle of the esophagus is more sensitive to adrenaline or epinephrine than is the circular muscle. Weak solns. of adrenaline increase the tonus and in some cases the rate and force of contraction of both muscular coats of the frog's stomach, small intestine, rectum and cloaca. Strips taken from different parts of the small intestine react to the same concn. of adrenaline in practically the same manner. The lower part of the alimentary canal, the intestine, rectum and cloaca appear to be more sensitive to adrenaline than the circular esophagus. Changes in the H-ion concn. of the Ringer bath due to the addition of adrenaline chloride do not alter the reactions of the tissues. 64 references are quoted.

C. J. WEST

Action of morphine on the vomiting center in the dog. C. D. LEAKE. *J. Pharmacol.*

20, 359-64(1922).—The action of morphine 1st stimulates and then depresses the vomiting center. It is suggested that this may be explained by reference to the reaction of reduced oxidation, as a result of the drug, upon the vital centers. C. J. WEST

Naturally nephropathic animals. The ability of an alkaline solution to influence the amount of stainable lipid material that appears in the kidney following the use of a general anesthetic. WM. DEB. MACNIDER. *J. Pharmacol.* 20, 365-84(1922).—The use of a soln. of Na_2CO_3 in naturally nephropathic animals causes an increase in the alkali reserve of the blood which may be maintained in an unanesthetized animal over a period of 2 hrs. at a point above the normal alkali reserve detn. for the animal. The use of such a soln. either so changes the character of the stainable lipid material normally present in the cells of the loops of Henle and in the convoluted tubule epithelium that it fails to stain with Scharlach R or the soln. causes the disappearance of such material from these cells. When naturally nephropathic animals are given a soln. of NaCl and then anesthetized with Et_2O for a 2-hr. period, the animals are found to be unable to maintain during the anesthesia a normal alkali reserve of the blood. There occurs a reduction of the alkali reserve of the blood and urine formation is reduced or the animals become anuric. With Na_2CO_3 , however, most animals maintain a normal alkali reserve of the blood and the kidneys of such animals fail to show the presence of stainable lipid material in the cells of the loops of Henle or in the convoluted tubule epithelium. The animals remain freely diuretic and responsive to a diuretic substance, theobromine. In those animals that were unable to maintain a normal acid-base equil. of the blood, lipid material stainable with Scharlach R was present in the above-mentioned cells. This indicates a relation between the amt. of stainable lipid material in the renal epithelium and the toxicity of the anesthetic for the kidney. C. J. W.

Picrotoxin hyperglucemia. A. L. TATUM. *J. Pharmacol.* 20, 385-92(1922).—Picrotoxin is a centrally acting glycogenolytic agent effective in subconvulsant dosage. It does not act to produce hyperglucemia in animals with denervated adrenal glands which fact indicates their necessary intervention in the production of picrotoxin hyperglucemia. C. J. WEST

Action of quinine on sugar mobilization with its bearing on the question of glycogenolysis. A. L. TATUM AND R. A. CUTTING. *J. Pharmacol.* 20, 393-403(1922).—Quinine properly administered is a glycogenolytic agent. Its hyperglucemia is the result of a central nervous system disturbance which leads by way of the splanchnic nerves and the normally innervated adrenal glands to lysis of glycogen. In the absence of adrenal innervation quinine produces in most instances hypoglucemia, most likely by virtue of a peripheral depression of glycogenolysis. Quinine produces in most instances examd. a rise in alk. reserve capacity of whole blood along with hyperglucemia in normals and hypoglucemia in animals with denervated adrenal glands. Neither quinine nor epinephrine hyperglucemia can, on the basis of available evidence, be considered dependent on acidosis. C. J. WEST

Preparation of hatters fur (JOHNSON) 25. Gas intoxication in Röntgen rooms (LOENNE) 7.

I—ZOOLOGY

R. A. GORTNER

A method of examination of the chemical sense with low animals and some results obtained with Daphnia. F. J. J. BUYTENDIJK. *Physiol. Lab. Free Univ. Amsterdam. Arch. néerland. physiol.* 7, 116-25(1922).—To study the chem. sense of lower animals, the statistical method, applied so far, does not furnish satisfactory results. B. observes the movements of a single Daphnia. A dish, 4.5 cm. in diam., is covered with black

paper on the outside and placed on a ground glass plate, illuminated uniformly from below. The round basis of this dish is divided into 4 quadrants. The movements of the animal are observed during 5 to 10 min. from above and drawn with chinese ink on a glass plate. If no substance with a sp. physiol. action is present the *Daphnia* will move uniformly through the 4 quadrants. If a substance, having a sp. chemotropic action, is introduced by means of a capillary into one of the quadrants the animal, in making its irregular movements, will either avoid this quadrant (in case of negative chemotropism) or prefer it (in case of positive chemotropism). A number of substances are examd. by that method. Negative chemotropism is found for NH_3 , NaOH , HCl , the lower fatty acids (formic acid, acetic acid, butyric acid, valeric acid, and caprylic acid) while the higher fatty acids (heptylic, octylic, decylic, undecylic), and the still higher ones are positively chemotropic. Observing the action of a series of homologous alcs., the reverse statements are made: the lower ones (methyl, ethyl, butyl, and amylalc. (are positive, the higher ones) octyl, nonyl, undecylalc.) are negative. Odorous substances, like bornyl acetate, are also positively chemotropic, and also such substances, as milk or bread, which serve as food for the animals.

R. BEUTNER

The non-protein organic constituents in the blood of marine fish. W. DEMIS. *J. Biol. Chem.* **54**, 693-700(1922).—By using the methods of Polin and Wu (*C. A.* **13**, 2541) for non-protein N, urea, creatinine, creatine and glucose, of Polin (*C. A.* **16**, 1789) for amino N and of Benedict (*C. A.* **16**, 2524) for uric acid (direct method), the following figures were obtained with 3 elasmobranch fishes (dogfish, dusky shark, sand shark): non-protein N 1000, urea N 800, amino N 28, creatinine 6, creatine 25 and uric acid 1.1 mg. per 100 cc. blood. In 4 teleost fishes (sculpin, tautog, cunner and menhaden), the values were non-protein N 65, urea N 9, amino N 28, creatinine 1.0, creatine 6 and uric acid 4 mg. per 100 cc. Although the muscle tissues of *Limulus* and the lobster contained 15.6 and 40 mg., resp., of amino N, per 100 g. of tissue, the blood of the former contained none and that of the latter only 3.3 mg. The blood sugar content was from 80 to 100 mg. per 100 cc. and was greatly increased by partial asphyxia (in the dogfish).

I. GREENWALD

Comparative studies of digestion. I. The digestive enzymes of celenterates. M. BODANSKY AND W. C. ROSE. *Am. J. Physiol.* **62**, 473-81(1922).—The following enzymes are present in the jelly fish *Stomolophus meleagris* and in the Portuguese-man-of-war *Physalia arethusa*: pepsin, trypsin, rennin, amylase, maltase and lipase. Invertase is present in negligible amt. Inulinase and lactase are absent. Proteins naturally used as food (fish) are more readily hydrolyzed than are proteins foreign to the customary diet (egg albumin, beef, fibrin and casein), suggesting a sp. adaptation of the enzymes to the individual proteins upon which they customarily act. **II. Digestion in elasmobranchs and teleosts.** *Ibid* **62**, 482-7(1922).—A peptic enzyme, having a max. activity at a pH of about 3.0, was demonstrated in the gastric mucosa of the elasmobranchs *Squalus acanthias* (dogfish), *Pristis pectinatus* (sawfish), *Torpedo galkani* (torpedo ray) and in the teleosts *Lutjanus aya* (red snapper), *Paralichthys lethostigma* (flounder), *Lactophrys tricornis* (cowfish) and *Mycteroperca bonaci* (black grouper). Fish pepsin effectively digests a larger variety of proteins than does the pepsin of either jellyfish or of Portuguese-man-of-war. Rennin is present in the stomach of the torpedo ray, red snapper, flounder and catfish; but absent in the dogfish, sawfish, cowfish and mullet. The pyloric caeca of the red snapper contain trypsin, pepsin, rennin, amylase, and lipase; inulinase, maltase and lactase are absent. The secretions of the pyloric appendages of the red snapper contain most of the enzymes which are usually found in the pancreatic juice of higher vertebrates.

J. F. LYMAN

Reproduction in cell communities. T. B. ROBERTSON. *J. Physiol.* **56**, 404-12 (1922).—Expts. with infusoria, *Enchelys farcinien*, lead R. to conclude that an autcata-

lytic substance, capable of synthesizing protoplasmic substance, originates in the cell nucleus. During cell division the autocatalyst is shared between the nuclear materials and the surrounding medium in a proportion detd. in part by its relative soly. and in part by its affinity for chem. substances within the nucleus. The nuclear membrane is then reformed, and the autocatalyst within the nucleus is again shut off from dispersal into the surrounding medium until the occurrence of the next succeeding division. The fact that a single cell cannot survive if isolated into too large a vol. of fresh culture medium is traceable to the excessive loss or dila. of the nuclear autocatalyst on cell division. The acceleration of cellular multiplication by almost any living tissue ext.—the "bios" effect of Wildiers—is due to the prevention of this drainage from the nucleus by previous satn. or partial satn. of the surrounding medium with the autocatalyst. Cf. C. A. 16, 759.

J. F. LYMAN

Variation of hydrogen ion concentration in the salt gardens as a biologic factor. ALPHONSE LABBÉ. *Compt. rend.* 175, 843-5(1922).—The numerous basins which are arranged in a salt garden so as to terminate in the crystallizers contain organisms of different species, the distribution of which has been attributed to the differences in salt concn. and consequent differences in osmotic pressure of the medium surrounding the organisms. It was observed that certain species live in basins of a detd. salinity, while in neighboring basins with an identical salinity the same species were few or absent. Believing that H-ion concn. might have an influence, p_H values were detd. by the method of Sørensen in the different basins. In the canals leading from the ocean to the salt gardens, p_H differed little from sea water, or 8.0 to 8.1, in the oozy places (vasières) it rises to 8.4, in basins with a concn. of 7 to 8° Bé. 8.4 to 8.5, with a concn. of 15 to 18° Bé. p_H rises to 9.2, but in basins of higher concn. p_H falls to 8.4-8.1. In these detns. it was necessary to allow for the "error of salinity" and the buffer action of the carbonates and bicarbonates present. **Distribution of animals in the salt gardens with relation to hydrogen ion concentration.** *Ibid* 913-5(1922).—There appears to be an intimate relation between the osmotic action of the cell or organism and the electric state of the membranes. Roughly stated, with concns. of salt below 7° Bé. and p_H 8.4, the organisms differed little from those of sea water. Concns. of 7-8° Bé. and p_H 8.4 to 8.6 gave a zone of *Idotea salinarum*; 12-18° Bé. and p_H 8.6-9.2-8.6 gave the zone of *Artemia salina*; 18-20° Bé. and p_H 8.6-8.3, the zone of *Fabrea salina*; and the crystg. basins at 27° Bé. and p_H 8.4-8.2, the zone of *Dunaliella salina*. While the compn. of the dissolved salts, the temp. and the viscosity of the soln. influence the life in the salt basins, the H-ion concn. appears to be the chief factor in causing differences in the distribution of life.

L. W. RIGGS

Osmotic pressure of the blood of "wiped" eels as a function of the modification of the salinity of the exterior medium. PAUL PORTIER AND MARCEL DUVAL. *Compt. rend.* 175, 1105-6(1922); cf. C. A. 16, 3673.—The eels were carefully wiped with a cloth, then placed either in 10 liters of ordinary water, or in the same vol. of water contg. variable amts. of added NaCl. The fish remained 3 hrs. in the soln., but every 45 min. they were removed, were carefully wiped and returned to the soln. In fresh water the osmotic pressure for the wiped eel is slightly below that for the normal eel. When by the addition of NaCl the f. p. of the soln. reaches -0.58° or lower, the f. p. of the serum of the wiped eel is always lower than that of the unwiped eel in the same medium. The removal of the mucus from the surface of the eel destroys an effective barrier which opposes exchanges between the external and internal mediums.

L. W. RIGGS

Soil reaction, water snails and liver flukes (ATKINS, LEBOUR) 15.

12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

Colloidal chemistry and the chemistry of foods. H. LÜERS. *Kolloid-Z.* **31**, 292-5(1922).—Colloidal chem. methods employed in the prepn. of certain food products, e. g., jellies and marmalades, are discussed. Adsorption phenomena are often responsible for the tastes of certain foods. A. A. CHRISTMAN

Preservation of foods by chemical substances. EMANUELE PATERNÒ. *Boll. chim. farm.* **61**, 769-70(1922).—The dangers attending the use of food preservatives are considered greatly exaggerated. Treatment of beef with formalin, although strictly prohibited in Italy, was nevertheless practiced on a large scale during the late war, and no harmful effects were observed. In Paris during the years 1877-8 some 300,000 kg. of meat preserved with H_3BO_3 were consumed without the slightest ill effect or even complaint; yet this preservative is now prohibited in France. P. suggests the appointment of an international commission to study the question of food preservatives with a view to abolishing unnecessary prohibitions. A. W. DOX

Penetration of heat in canned goods during sterilization. BIDAULT. *Bull. soc. hyg. aliment.* **10**, 471-86(1922).—Expts. gave practically the same results as those of Bigelow, *et al.* (*C. A.* **15**, 127). These results can be used in can. canning, so as to obtain reasonable certainty of efficient sterilization without unduly affecting the quality of the products. A. P.-C.

The value of boric acid canning compound in food preservation. MAX LEVINE. *J. Home Econ.* **15**, 64-70(1923).—A commercial canning compd. was found to be so ineffective against certain forms of organisms associated with food poisoning as to render its use with the directions accompanying it a distinct menace. L. D. ELLIOTT

Determination of refractive indices of milk in various concentrations and at various temperatures. GERDA MINNI. *Soc. Sci. Fennica Commentationes Physico-Math.* **1**, No. 16, 5 pp.(1922).— n_D of whole milk and of milk dild. with water were detd. at 5° intervals from 15° to 35°. BENJAMIN S. NEUHAUSEN

Chlorination of milk. R. A. MANSELL. *J. Roy. Army Med. Corps* **39**, 372-7(1922).—Milk may be kept fresh by addn. of bleaching powder soln. The Cl is not tasted when amts. of bleach soln. less than 2.5% of the milk vol. are added. The fat content is not appreciably affected. Infected milk may be rendered safe for consumption. The most commonly surviving organisms are *B. acidi lactici* and *B. lactis aerogenes*. A. T. CAMERON

Notes on the milk problem. HENRY LEFFMANN. *Am. J. Pharm.* **94**, 583-5(1922).—A review of methods for detecting adulteration, particular attention being given to the detection of added water by detn. of f. p. (*cf. C. A.* **15**, 1359, 3882).

W. G. GAESSLER

New biological method for the detection of the organs and flesh of horse. E. CÉSARI. *Rev. gén. méd. vét.* No. 366, 505(1922); *Ann. fals.* **15**, 481-2(1922).—The method is applicable to cooked as well as to raw products. Serum prepd. from rabbits which have been treated either with defibrinated sheep blood, or with cells of horse or sheep spleen, can hemolyze red blood corpuscles of sheep, and can also cause flocculation of colloidal emulsions obtained with previously heated alc. exts. of striated muscles, heart, lungs, kidneys, spleen, testicles, stomach, intestines, and mammary glands of horses, and blood and spleen of sheep. Detailed directions for prepg. the serum and for making the test are given. A. P.-C.

Determination of caffeine in tea and coffee. R. E. ANDREW AND E. M. BAILY.

Conn. Agr. Expt. Sta., *Bull.* 227, 256-8(1921); *Analyst* 46, 405.—Grind tea to pass $\frac{1}{16}$ inch sieve. To 5 g. tea in a 500-cc. graduated flask add 10 g. heavy MgO and 200 cc. H_2O . Boil gently over a low flame for 2 hrs. with a small-bore glass tube 30 in. long as a condenser. Cool, dil. to vol. and filter through a dry paper. To a 300-cc. aliquot in a 1. Erlenmeyer flask, add 10 cc. of 10% H_2SO_4 soln., evap. by gentle boiling to about 100 cc. Filter into a separatory funnel, washing the flask with small portions of 1% H_2SO_4 , and shake out 8 times with $CHCl_3$, using 25, 20, 15, 10, 10, 10-cc. portions. Treat the combined exts. with 5 cc. of 1% KOH soln. When the liquids have completely sepd. draw off the $CHCl_3$ layer. Wash the alk. soln. in a separatory funnel with 2 10-cc. portions of $CHCl_3$, and add the washings to the main bulk of the ext. Evap. or distil off $CHCl_3$ to a small bulk, transfer to a tared flask, evap. to dryness, and further dry in a water oven at 100° to const. wt. Transfer the residue to a digestion flask with successive small portions of H_2SO_4 and det. N by the Kjeldahl method. Calc. caffeine from N by the factor 3.464.

W. H. FRY

Eggs as a source of vitamin B. T. B. OSBORNE, L. B. MENDEL AND HELEN C. CANNON. *J. Am. Med. Assoc.* 80, 302-3(1923).—By extn. of egg yolk with water, it is possible to secure a product comparatively rich in vitamin B, the daily dose required for a 100-g. rat being considerably less than that of the most potent dried yeast hitherto examd. The content of the egg yolk in vitamin B is not large, a daily intake of at least 1.5 g. of the fresh yolk being required when it furnishes the sole source of vitamin to a 100-g. rat. The whole egg is accordingly not exceptionally rich in vitamin B, when contrasted with other foods already investigated. Judging by the comparative trials on rats, the av. sized hen egg is equiv. in vitamin B potency to about 150 cc. of cow milk.

L. W. RIGGS

The effect of cooking upon the vitamin content of cabbage. W. H. EDDY, ELIZABETH SHELLOW, RAMONA PEASE, MIRIAM RICHER AND LILLIAN WATKINS. *J. Home Econ.* 15, 15-30(1923).—Cooking in open vessels or pressure cookers destroyed between 90 and 95% of the vitamin C present in cabbage even with the addition of vinegar. Vitamins A and B apparently suffer little if any destruction in the usual cooking processes.

L. D. ELLIOTT

Silage studies. H. EDIN AND E. SANDBERG. *Medd. Centralanstalt. försöksväsen-det jordbruks.* No. 221, 1-90(1922).—Silage was made from red clover, timothy, peas, oats, barley, and Swedish turnip tops. Losses of org. matter ranged from 20 to 40%. Total acidity varied from 0.93 to 2.64% and lactic acid from 0.00 to 1.90%. In good silage no butyric acid was found; the lactic acid did not go below 0.78%; and the av. ratio between volatile acids and lactic was 1:0.88 with a variation between the ratios 1:1.77 to 1:0.44. In good silage 10 to 20% of the total N may be in the form of NH_3 and 22.8 to 45% in the form of peptones and amino acids. In silage with a comparatively low total acidity and a high proportion of volatile acids the pure proteins have undergone deep-seated decompn. Absence of peptones and amino acids indicates a poor quality of silage. Digestibility studies were made.

C. O. SWANSON

Feeds containing molasses. ROTHÉA. *Ann. fals.* 15, 339-53, 408-19, 464-70 (1922).—The quality of these feeds depends on the nature and amt. of molasses and of base. The nutritive value of the molasses depends on its sugar content; but the ash content must also be taken into consideration owing to the large proportion of K_2O , which is toxic when ingested in large quantities. A large number of analyses of bases (various straws and brans, cocoa shells, etc.) and of prepd. feeds are given and commented on. The methods of analysis used are given, and recommendations are made as to the regulation of the sale of these feeds.

A. P.-C.

Nutritive value of certain Australian grasses. MARGARET H. O'DWYER. *Proc. Linnæan Soc. N. S. Wales* 47, 516-8(1922).—A previous paper (C. A. 16, 299) gave re-

sults based mainly on the examn. of the first stage of growth of each grass. Similar data are now given relating to the 2nd (early flowering period) and 3rd stages (seed quite set.) A. P.-C.

Stock feeding. P. DE SORNAY. *Rev. agr. Maurice* 1, 244-6(1922).—A table of analyses of plants used for feed in Mauritius is given, including nutritive ratios based on digestibility factors employed in the U. S. F. W. ZERBAN

Determination of chlorides in foodstuffs (RUSZNYAK, KELLNER) 11B. Apparatus for drying fruits, vegetables, etc. (U. S. pat. 1,442,179) 1. Apparatus for sterilizing (foods) by impact (U. S. pat. 1,440,868) 1. Dry granular acid calcium phosphate (U. S. pat. 1,442,318) 18.

CLARKE, A.: **Flavouring Materials: Natural and Synthetic.** London: Henry Frowde and Hodder and Stoughton. 166 pp. 8s. 6d.

GREENISH, HENRY G.: **The Microscopical Examination of Foods and Drugs.** 3rd Ed. Revised. London: J. and A. Churchill. 386 pp. 18s. Reviewed in *Pharm. J.* 109, 562(1922).

SPICA, P.: **Chimica bromatologica.** 2nd Ed. Padua: La Litotipo. 294 pp. L. 30.

Food from waste meat. P. HILDEBRANDT. U. S. 1,442,339, Jan. 16. Food products resembling "Liebig's meat ext." are prepd. from waste meat, cartilage, sinews, horn, hair and skins by gradually adding successive portions of the material to an aq. acid soln. and heating. Each portion of material is brought into soln. before the next portion is added and the time required for this varies with the strength of acid used. According to U. S. 1,442,340, the disagreeable taste often inherent in such preps. is avoided by preliminarily treating the raw material with live steam or with solvents such as C_6H_6 , ether or alc. before subjecting it to hydrolysis, or by such prolonged boiling as to effect distn. of the unpleasant substances with steam. U. S. 1,442,341 specifies treatment of raw materials such as horn with a dil. Na_2CO_3 soln. or other alk. soln. after heating the material to 100° , draining off the soln. and then hydrolyzing the material with either dil. acids or dil. alkalies to obtain a food product free from bad odor or taste.

Alcoholic solutions of proteins. D. THOMSON. Brit. 174,433, Oct. 23, 1920. A substance rich in undigested animal protein, *i. e.*, minced lean meat, is treated with a dil. alkali and filtered, the filtrate being then slightly acidified. The protein thus pptd. is filtered off, redissolved in dil. acid, and mixed with an alc. liquid such as whisky, brandy, or sherry. The product may be flavored with oil of lemon or capsicum. In the treatment of the meat with alkali such as Na_2CO_3 soln., the mixt. may be mechanically stirred and heated to not more than 40° . It may be strained through fine muslin; a centrifugal separator may be used, and the liquid may finally be filtered through asbestos wool. HCl or glycerophosphoric acid may be used for dissolving the pptd. protein. According to the provisional specification, NaOH is used instead of Na_2CO_3 .

Coagulating milk. WARD BAKING CO. Brit. 186,925, Oct. 3, 1922. Milk is coagulated by adding an enzyme produced by the growth of *Mucor rouxii* on a suitable medium such as rice. The rice is cooked in H_2O or a mixt. of milk and H_2O , cooled and inoculated with spores of the fungus. Access of air to the mass is restricted if it is desired to minimize formation of spores in order to avoid a dark coloration of the rice. The product may be prepd. in powd. form by grinding the rice, or the enzyme may be extd. with H_2O , and the liquid, which may be concd. at a low temp., may be used in liquid form or sprayed on rice flour or other absorbent material.

Preserving milk. S. J. DAVIS. U. S. 1,436,947, Nov. 28. Cow or goat milk is freed from foreign matter by centrifuging and quickly heated to about 82–85° and maintained at this max. temp. for about 1 min. only, immediately cooled to about 65° and at this temp. is homogenized under a pressure of 3000–3500 lbs. per sq. in. to increase digestibility and preclude sepn. of the constituents of the milk even when kept for a long time. (A homogenizing app. adapted for this purpose is described). After coming from the homogenizer, the milk is cooled to about 10° and sealed in cans or bottles, quickly heated to 110° to effect sterilization and then cooled.

Apparatus for ripening milk or cream. J. T. HANNA and L. E. COON. U. S. 1,442,336, Jan. 16. Pipe connections are provided for passing heated air through milk or cream in a ripening app.

Apparatus for electric sterilization of milk or other liquids. H. B. RUDD. U. S. 1,432,124, Oct. 17. The liquid to be sterilized is passed through an angular receptacle opposite sides of which are formed by electrodes.

Bread-making. R. GRAHAM. Brit. 187,935, Nov. 18, 1921. In bread-making from cereal and soy-bean flours, the unpleasant taste of the soy bean is removed by using a large amt. of yeast, or by using a yeast food such as inactivated yeast, sugars (glucose, levulose, cane-sugar, or molasses sugar), rye or buckwheat flours, and fermenting. Examples of suitable proportions are given, the doughs being fermented for 1 or 1½ hr., at a temp. of 20°. When rye flour is used it is mixed with yeast and H₂O and, after ¾ of an hr., is kneaded with the other materials. When old soy-bean flour is used, additional rye or buckwheat flour is added or the ebullition point of the liquid in the dough is raised by increasing the content of crystalloid solubles, i. e., salts, sugars. Cf. C. A. 16, 2372.

Bread-making. WARD BAKING CO. Brit. 186,923, Oct. 3, 1922. Relates to a bread-making process of the type described in 156,635, the fungus used in the present invention being *Mucor rouxii*, which is preferably grown on rice, swollen to twice the original size by cooking in an open vessel with boiling water in the wt. proportions of 100 parts of rice to 75 parts of water and cooling to 35°. A seeding stock is used which is prepd. by growing *Mucor rouxii*, in a moist atm., on cooked rice contg. 75% of H₂O, slowly drying the rice and mycelium, while the mass assumes a dark color due to the formation of spores, and grinding to a powder. The mixed rice and seeding stock are spread on trays in layers from 1 to 3 in. in thickness. The enzyme product may be extd. with H₂O, which does not ext. the color of the spores, and in this case sporulation is stimulated by allowing air circulation through the mass, which is kept in a room with a moisture-laden atm. at a temp. of 25–40°, preferably 35°, from 1½ to 3 days. The enzymes may be dissolved out of the cake-like mass before or after drying and the soln., with or without concn., used in the dough batch. The cake-like mass may be used in powder form, in which case sporulation and consequent discoloration are restricted by preventing the air circulation with tray covers and lengthening the period of growth. The mass is dried by heat, in air or a vacuum at a temp. not exceeding 75° and ground to a meal which will pass through a mesh of 100–200 to the in. The meal may be used in the proportion of from ½ to 2 lbs. to 1000 lbs. of flour and the other ordinary ingredients. Both the soln. and meal contain sugar produced by the action of diastatic enzymes on the rice starch, which sugar contributes in making up the normal amt. of sugar used. In the sponge process the meal is added, at the sponge stage, to the flour, water and yeast. Compare C. A. 17, 837.

Cereal germ preparations. WARD BAKING CO. Brit. 186,634, Oct. 2, 1922. A product that may be eaten by itself or used as an ingredient in bread or cereal foods, infants' foods, etc., confectionery, or ice-creams is made from products such as "rice polishings" or other milling refuse contg. cereal germs, such as wheat or maize germs.

The germs, with which ground roasted peanuts may be mixed, are freed from oil by a solvent, such as C_6H_6 or CCl_4 , the oil being used for making soap. The germs are then cooked to gelatinize the starch, which is saccharified by means of an infusion of malt. They are then treated with digestive enzymes, such as papain, trypsin, pancreatin and pepsin, acid being added if necessary. The action is stopped by boiling and the resulting liquid filtered and concd. or evapd. to dryness. Alfalfa may be added to the germs. Either the treatment with malt or that with digestive enzymes may be omitted, the latter being sometimes preferable when the product is to be used for bread. The starch may be hydrolyzed by acids instead of malt, when the treatment with digestive enzymes precedes the hydrolysis. The germs may be extd. with H_2O or alc. without preliminary treatment, or after extn. of oil only, and the ext. concd.

Treating flour, etc. NAAMLOOZE VENNOOTSCHAP INTERNATIONALE OXYGENIUM MAATSCHAPPIJ "NOVADEL." Brit. 186,940, Oct. 9, 1922. Flour or milling products are bleached and improved by the addn. of "peraldehydes," ozonides, or "perozonides" or mixts. or derivs. thereof either before, during or after the milling process. Detrimental enzymes, etc., may be destroyed previously by treatment with active Cl or a material yielding Cl. Peroxides, persalts, other per compds. or moisture may be added and the mixt. may be subjected to chem. or phys. treatment to assist the action of the added substance, e. g., by exposure to ultra-violet rays.

Enzymes. WARD BAKING CO. Brit. 186,924, Oct. 3, 1922. In producing diastatic and proteolytic enzymes for use in bread-making by cultivating a fungus, especially *Aspergillus oryzae*, on a cereal medium such as hominy boiled in H_2O , acid is added to the culture medium to inhibit the growth of organisms which produce "ropiness." The invention is particularly described with respect to lactic-acid; a mixt. of lactic and citric acids is also mentioned as suitable. In prepg. the seeding stock a smaller proportion of H_2O is used than in producing the enzyme, and common salt is added.

Condiments. WARD BAKING CO. Brit. 187,612, Oct. 18, 1922. Yeast is boiled under a pressure of about 30 lbs. to the sq. in., so as to rupture the cells; the filtrates are filtered and evapd. to dryness, and ground. Salt may be added. The evapn., which is preferably effected *in vacuo*, should be stopped when the concentrate is of light brown or yellowish brown color. The substance should be ground and packed while still hot to prevent it from absorbing moisture.

Treating fruit, vegetables, etc. PLAUSON'S (PARENT CO.) LTD. Brit. 186,756, July 30, 1921. Fruit, vegetables, etc., are made into colloidal dispersions in H_2O or other liquid by a mech. process such as that described in 155,836; undesired constituents may be pptd. and the soln. concd. or dried. When grapes are treated, the cellulose may be coagulated by boiling or by the use of alc., which may be added or produced by fermentation. Apples may be treated and the juice freed from cellulose by boiling, mixed with sugar and evapd. to form a conserve. In treating beets, impurities may be coagulated by boiling and sugar sepd. in the ordinary way. Cacao beans may be treated and the soln. heated to 60-80° to coagulate cellulose, lignin, etc. The soln. is concd. by drying with or without sugar and a protective colloid such as gelatin or Iceland moss, and the dry product pulverized. Fat, etc., may be added and the mass worked up into chocolate.

Emulsions. E. V. SCHOV. Brit. 187,299, July 12, 1921. Permanent emulsions of the kind in which the internal and external phases are constituted by aq. liquid and oleaginous material, resp., are formed from oleaginous materials which themselves possess H_2O -dispersing properties. These properties are acquired by heating or polymerizing the oleaginous materials without oxidizing them, or by heating or polymerizing after or with simultaneous oxidation, whereby the oleaginous material becomes gelatinated, sticky and elastic, such processes being generally known. This treated

material may be directly emulsified with the aq. liquid, or it may be dild. with a quantity of untreated material; the mixt., which also possesses H_2O -dispersing properties, may be subsequently emulsified. The aq. liquid may contain a little solid matter of a sticky nature, e. g., glue or casein., and is added to the oleaginous material during vigorous stirring. The resulting emulsion is sol. in oil and is particularly useful in *painting and priming* materials as described in 175,764 (C. A. 16, 2233), or in the *manuf. of margarine or edible fats* as described in 178,885 (C. A. 16, 3517).

Oleaginous compositions. E. V. SCHOU. Brit. 187,298, July 12, 1921. Oils contg. linolic, linoleic, or linolenic acids, such as linseed, soy, cottonseed, sesame, and ground-nut oils, are gelatinized by polymerization or oxidation, or both, and then dissolved in further quantities of oils or fats. E. g., air or superheated steam is blown through 100 parts of soy oil heated to 250° , the volatile products being recovered by condensation. When gelatination occurs the oil is cooled to 100° and 300 parts of cottonseed, ground-nut, or sesame oil are mixed with it. The resulting soln. may be used as a *substitute for butter or lard* for baking purposes, as an addn. to oils and fats for increasing their viscosity, or in the prepn. of emulsions, which may be used in the manuf. of margarine and edible fats. Cf. 175,764 (C. A. 16, 2233), 178,885 (C. A. 16, 3517), and 187,299 (above).

Fodder from straw. E. BECKMANN. U. S. 1,442,321, Jan. 16. Straw or similar material is chopped into small pieces and treated with an alk. soln. at a temp. of 40 – 60° for 3–12 hrs. to prep. fodder. U. S. 1,442,322 specifies treating the chopped material with a 0.5–2% soln. of alkali at a temp. of about 20° for about 3 hrs.

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

Suggested definitions relating to methods of testing. J. A. CAPP, *et al.* *Proc. Am. Soc. Testing Materials* 22, I, 516–20(1922).—Numerous definitions are recommended relating to mech. testing. A method for constructing stress-strain diagrams is described and illustrated.

C. C. DAVIS

Report of committee E-1 on methods of testing. J. A. CAPP, *et al.* *Proc. Am. Soc. Testing Materials* 22, I, 501–15(1922).—A classification of all methods of testing in 16 divisions is given. Progress in the revision of methods of testing is outlined.

C. C. DAVIS

Suggested methods for verification of testing machines. J. A. CAPP, *et al.* *Proc. Am. Soc. Testing Materials* 22, I, 521–33(1922).—Definitions, methods for verifying the accuracy of machines and tolerances are given.

C. C. DAVIS

Report of committee E-8 on nomenclature and definitions. C. M. GHAPMAN, *et al.* *Proc. Am. Soc. Testing Materials* 22, I, 539–49(1922).—Recommendations for definitions of materials and properties.

C. C. DAVIS

Report of committee D-9 on electric insulating materials. F. M. FARMER, *et al.* *Proc. Am. Soc. Testing Materials* 22, I, 472–8(1922).—Recommendations for slight changes in present tentative methods and an outline of work during the yr.

C. C. D.

Report of committee D-8 on waterproofing materials. C. N. FORREST, *et al.* *Proc. Am. Soc. Testing Materials* 22, I, 468–71(1922).—It is recommended that several specifications published in 1920 be slightly revised.

C. C. DAVIS

Some achievements of chemical industry during the war in this country [England] and in France. WM. MACNAB. *J. Soc. Chem. Ind.* 41, 353–61T(1922).—Hurter Memorial Lecture. M. sketches interestingly the growth of the Brit. and French plants and

processes during the war years, in which picric acid, TNT, oleum, NH_4NO_3 and other war-required chemicals were produced. Photographs of picric acid processes and graphs to illustrate statistics accompany the article.

E. G. R. ARDAGH

Influence of pulsations on the reactions of gases in the presence of packings. JULES DESCHAMPS. *Chimie et industrie* 8, 1167-71 (1922).—A general discussion clearly showing the advantages of pulsations over steady flow in causing proper motion and mixing of the gases instead of eddies in some parts and stagnation in other parts of the gas mass.

A. P.-C.

Accelerated reactions in pulsating gaseous currents. JULES DESCHAMPS AND J. F. SHADGEN. *Chem. Met. Eng.* 27, 1269-71 (1922); cf. preceding abstr.—Pulsation is applicable in cooling, volatilizing, concg. or distg. app. The nature of the pulsations desired depends upon the effective height of the checkerwork or filling, upon the dimensions of the solids or bricks, and upon the speed of reaction characteristic of the chem. and phys. phenomena involved.

W. H. BOYNTON

Effect of agitation on the rate of solution of crystals. E. V. MURPHREE. *Ind. Eng. Chem.* 15, 148-9 (1923).—If V = vol. of soln., θ = time, c_s = concn. of satd. soln. as wt. per unit vol., c = concn. of soln. at time θ in same units, x_0 = linear dimension of crystal at zero time, x = linear dimension of crystal at time θ , W_0 = total wt. of crystals at time zero, W = total wt. of crystals at time θ , n = no. of crystals = W_0/ax_0^3 , ax_0^3 = wt. of one crystal, bx_0^2 = surface of one crystal, and a and b are consts. the numerical value of which depends upon the form of the crystal grains, then the time necessary to dissolve a given crystal is as follows: $n(ax_0^3 - ax^3) = Vc_s$. Exptl. work seems

$$\frac{Vb}{na} \left[\frac{1}{2} \ln \frac{(k+x_0)^2 (k^2 - kx + x^2)}{(k+x)^2 (k^2 - kx_0 + x_0^2)} + \sqrt{3} \tan^{-1} \frac{k\sqrt{3} (2x_0 - 2x)}{3k^2 + (2x_0 - k)(2x - k)} \right] = K\theta$$

to confirm this equation. In the special case of a quantity of salt so large that the change in its surface during soln. is negligible, the above equation reduces to $\ln(c_s/(c_s - c)) = KB\theta/V$.

W. L. BADGER

Glass rings. A new filling material for towers. F. C. ZEISBERG. *Chem. Met. Eng.* 28, 9-10 (1923).—The properties of glass rings, 12 × 12 mm. and smaller, are given. They are recommended for filling small, plant-scale rectifying columns.

F. C. Z.

Experiments with the Suthau oil-testing machine. K. HASSEL. *Chem.-Ztg.* 46, 992-3 (1922).—The oil-testing machine of E. Suthau, Cologne, is driven at a const. speed, under a const. bearing-pressure, the journal and bearing being of a character comparable with that of a commonly used type. The no. of revolutions which are necessary to raise the temp. of the bearing 1° (or 50°) is detd. Deflections of a pendulum attached to the bearing are observed also. Three drops of oil is sufficient for a test. About 40 oils were tested by H. in accordance with the directions furnished by Suthau. Duplicate runs with the same oil checked within $\pm 2\%$. However, the results were of no practical value. Several oils from different sources, the viscosities of which varied considerably (21.9-26.9 Engler degrees at 20°, and 3.9-4.3 Engler degrees at 50°) gave nearly identical results with the Suthau machine. Suthau reported quite different results from a series of oils of much more nearly the same viscosities. H. considers that two oils of the same class may give the same test on the Suthau tester, although one may require minimum power at 30°, while the other may require a minimum at 50°.

W. F. FARAGHER

Lubrication by emulsion. GREGOR HARTMANN. *Chem. Weekblad* 20, 59 (1923).—Water satd. with CaO is emulsified with 3 times as much of lubricating oil. This mixt. is used for oiling cylinders of steam engines. The waste of oil is, in that way, reduced considerably.

R. BEUTNER

HAHN, HANS: *Grundriss der Chemie für Techniker*. Vol. I. *Anorganische Chemie*. 2nd Ed. 193 pp. M 50.

HEMPPELMANN, ALBERT: *Betriebsverrechnung in der Chemischen Grossindustrie*. Berlin: Julius Springer & Co. 107 pp. 5s. 6d.

HYDE, J. H.: *Lubrication and Lubricants*. London: Isaac Pitman & Sons. 114 pp. 85 cents. Reviewed in *Mech. Eng.* 45, 148(1923).

KEMPTON, P. H. S.: *Industrial Applications of X-rays*. London: Isaac Pitman & Sons. 112 pp. 2s. 6d. Reviewed in *Mech. Eng.* 45, 148(1923).

KRAUSE, HUGO: *Chemisches Auskunftsbuch für Fabrikanten, Gewerbetreibende u. Landwirte*. 2nd Ed. revised and enlarged. Vienna and Leipzig: A. Hartleben. 254 pp.

ROBINSON, CLARK S.: *The Recovery of Volatile Solvents*. New York: The Chem. Catalog Co. 188 pp. \$2.50. Reviewed in *J. Franklin Inst.* 195, 141(1923).

THORPE, EDWARD: *A Dictionary of Applied Chemistry*. Vol. IV. Revised and enlarged. London: Longmans, Green & Co. 740 pp. 60s. Reviewed in *Pharm. J.* 109, 562(1922).

Nuova enciclopedia di chimica scientifica, tecnologica et industriale con le applicazioni a tutte le industrie chimiche et manifatturiere, ecc. Founded and directed by ICILIO GUARESCHI and finally under the direction of FELICE CARELLI. Vol. X (Oss-Q). Turin: Unione Tipografico-Editrice Torinese. 1252 pp. L. 95.

Removal of solid and liquid particles from gases (Nesbit) 21. Removing vapors from dye-houses, etc. (Springer) 25. Plastic composition (for insulators)(Brit. pat. 187,376) 18. Laminated sheets comprising phenolic condensation products [for making electric insulators](U. S. pat. 1,441,133) 18.

Evaporating liquids. T. RIGBY. Brit. 187,260, May 10, 1921. In evapg. liquids in multiple-effect app. particularly of the kind described in 180,963 (C. A. 17, 842) in which the liquid is fed in parallel to the effects, the liquid is passed in series through a no. of multiple-effect plants, the temp. ranges of which coincide or overlap substantially. In concg. brine or other liquid the b. p. of which rises on evapn., the first effects of each plant are preferably supplied with steam from the same source and the last effects are connected to the same condenser, and the no. of effects in each succeeding plant is progressively diminished. In evapg. cane or beet sugar solns., the concn. obtained in the last plant may be such that crystals sep. in the effects of this plant, or crystn. may be effected outside the plant in crystg. vessels which may be supported on wheeled devices or in heated pans in which slow evapn. takes place. When the concd. liquid is to be cooled to cause crystn. or for other purposes, the vessel contg. the liquid is connected to the vapor spaces of effects at progressively lower pressures so as to cause the liquid to flash off steam and to lower the temp. in stages. The method of cooling the concentrate, and recovering the heat for use in the evapg. process may be used in a plant in which the multiple-effect app. is replaced by app. of the kind described in 12,462, 1911 (C. A. 6, 3039), in which the vapors evolved on evapn. are compressed and used as the heating agent. In concg. impure liquids such as sea water, which at one stage of the concn. will deposit impurities, such as CaSO₄, etc., on cooling, the cooling may be effected by flashing-off vapors from the soln. by connection with effects of lower pressure during the passage of the soln. from one evapg. plant to the next. The soln. may be preheated before passage into the next plant by heat-exchange with the soln. from the first plant. According to one provisional specification the control device described in

180,963 (C. A. 17, 842) for controlling the passage of vapor from one effect to another may be used also to control the inflow of liquid into the effect.

Evaporating liquids generating acid vapors. H. A. E. NILSSON. U. S. 1,440,026, Dec. 26. In evap. *sulfur waste liquors* or other liquids generating acid vapors in an app. in which compression of the vapors is utilized for heating the evaporator, the vapors are scrubbed with milk of lime or otherwise treated to eliminate acid before being brought into contact with metal heating elements which might be damaged by the acid.

Controlling foaming of boiling liquids. C. E. DOLBEAR. U. S. 1,440,973, Jan. 2. Excessive foaming of boiling liquids, *e. g.*, brines contg. K salts, is prevented by the addn. of petroleum distillate and by generation of Cl in the soln. electrolytically.

Reacting on solids with gases. O. NYDEGGER. U. S. 1,440,620, Jan. 2. Exothermic reaction between gases and solids, *e. g.*, *chlorination of lime*, is controlled by cooling a portion of the gas in a circulating current before it enters the reaction zone. An app. is described.

Fine powders by precipitation from gases. W. K. LEWIS. U. S. 1,442,485, Jan. 16. In pptg. fine powders from gases, *e. g.*, ZnO or a sulfide of As or Sb, the gaseous material is highly divid. with combustion gases or other inert gas to facilitate obtainment of the pptd. solid material in very finely divided form.

Storing gases and inflammable liquids. E. E. PETITPIERRE. Brit. 187,600, Oct. 13, 1922. Compressed or dissolved gases, *e. g.*, C₂H₂ dissolved in acetone, or inflammable liquids are stored in containers filled with peat which may be untreated or ground or otherwise treated and may be mixed with other fibrous or porous material.

Storing oxygen or other gases. M. H. ROBERTS. U. S. 1,439,911, Dec. 26. The gas, *e. g.*, O from liquid-air rectification, is compressed in contact with H₂O and substantially all the moisture is sepd. from the gas by refrigeration before the gas is led to a storage receptacle.

Propane as a refrigerating agent. A. G. CRAWFORD. U. S. 1,439,728, Dec. 26. Evapn. of liquefied propane is utilized for refrigeration in ice making, cold storage or general refrigerating systems. Cf. C. A. 16, 600, 1998.

Plastic packing for stuffing boxes. D. STERNLIER. U. S. 1,441,951, Jan. 9. Rape or colza oil 4, chalk 18, flaky graphite 5 and spongy grains of bearing metal 100 parts.

Laminated heat-insulating fabrics containing asbestos, cat hair or other fiber and adhesives. J. DeLONG. U. S. 1,442,325-6-7-8, Jan. 16.

Molded electrical insulators. L. E. BARRINGER. U. S. 1,439,991, Dec. 26. Molded insulators, etc., are formed from shredded sheet asbestos, wood or cotton treated with shellac, bakelite or other suitable thermoplastic binder.

Electrical insulation. P. E. DEMMLER. U. S. 1,440,448, Jan. 2. An elec. insulating material in thin sheet form is formed by coating metal foil (Pb 85 and Sn 15%) with a self-sustaining film of baking varnish, *e. g.*, an ordinary insulating varnish, drying the latter and stripping it from the foil in a bath of paraffin and carnauba wax.

Uniting parts of line insulators. A. F. E. BÜLTEMANN. U. S. 1,440,003, Dec. 26. A plastic mixt. of port. cement and asphalt is fused between insulator parts after setting.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

The stability of a 0.01 N sodium oxalate solution. EDW. S. HOPKINS. *Ind. Eng. Chem.* 15, 149(1923).—(CO₂Na)₂ soln. used for H₂O analysis deteriorated considerably after 1 week. After 17 weeks only 74% as much KMnO₄ was required. Addn. of 100 cc. of 1 : 4 H₂SO₄ per l. of (CO₂Na)₂ prevented for at least 2 mos. any deterioration,

even when in clear glass bottles in daylight (cf. Treadwell and Hall, *Quantitative Analysis*, 599).

C. C. DAVIS

The use of planktological methods for the identification of pathogenic bacteria in water. J. WILHELM. *Desinfektion* 4, 81-3(1922); *Wasser u. Abwasser* 17, 243(1922).—W. proposes the use of plankton nets to remove suspended matter from polluted water, with subsequent examn. of shreds of cloth or paper, starch cells or muscular fibers for adhering pathogenic bacteria.

F. W. MOLHMAN

The storage of water samples before bacteriological examination. HAROLD HUSS. *Gas u. Wasserfach* 15, 238-9(1921); *Wasser u. Abwasser* 17, 244(1922).—H. claims that Swedish conditions permit an interval of 4 hrs. between sampling and plating, without icing. If kept under 9° the sample may be stored 48 hrs., if under 5°, 72 hrs.

F. W. MOLHMAN

The dangers of drinking water of bad quality. A. REICH. *Wasser* 13, 21-4(1922); *Chimie et industrie* 8, 1245(1922).—Brief general discussion of the dangers of metallic and bacterial contaminations, with a description of the development of epidemics.

A. P.-C.

Water supplies with reference to those in the Gallipoli campaign. A. GASKELL. *J. Staff Med.* 31, 15-27(1923).—The work of the Royal Naval Division in Gallipoli during the World War is outlined. The importance of good organization, administration, education and discipline is emphasized. The H₂O supplies were mainly shallow wells except Ramona's Spring. The wells were grossly polluted but the spring furnished a H₂O of good quality. The Mark V. water cart was largely used. The cart has a 110 gal. tank into which H₂O is pumped through a clarifying and chlorinating cage. Clarification is accomplished by the formation of a film of Al(OH)₃ on a cloth and its object is to produce a condition in which the dosage of Ca(OCl)₂ shall be const. Sterilization with NaHSO₄ tablets, although it gave a safe water, was discarded since the water was unpalatable; special water bottles were also required as free acid acts on the metal. Cl tablets are not to be recommended. Owing to the lack of water carts, etc., water borne disease was not largely prevented in Gallipoli.

G. C. BAKER

Poison gases and water supply. THIESING. *Wasser u. Gas* 12, 305-9(1922); *Wasser u. Abwasser* 17, 254(1922).—Mustard gas can be removed from water by boiling 1/4 hr. or by storage for 8 or 9 days at 12°. Phosgene is quickly decompd. by H₂O. As compds. are usually associated with HCN and are not removable by boiling. Chloropicrin is insol. in H₂O. Chem. methods for removal of poison gases are not satisfactory.

F. W. MOLHMAN

The effect of polarized mercury in locomotive boilers. GEO. L. FOWLER. *Railway and Locomotive Eng.* 35, No. 10(1922).—Formation of black magnetic oxide of iron on tubes of boilers using Bird Archer compd. is attributed to the presence of metallic Hg in the compd.

R. C. BARDWELL

Economies of water service for railway locomotives. C. H. KOYL. *Railway Age* 74, 275(1923); cf. C. A. 17, 166.—Results of water treatment on completely treated engine districts of the C. M. and St. P. R. R., and the Great Northern Railway indicate a saving of \$1000 per mile of road or approx. \$4000 per engine over costs of operation with the untreated water.

R. C. BARDWELL

Water treatment justified by results secured. W. C. SMITH. *Railway Age* 74, 277(1922).—Mo. Pac. R. R. obtains excellent results from 81 water treating plants making a net annual saving of \$500,000. An outline of organization and method of handling treatment is given.

R. C. BARDWELL

The chlorine value of water and sewage. V. FROBOESE. *Arb. Reichsgesundh.* 52, 211(1920); *Wasser u. Abwasser* 17, 269(1922).—The Cl-combining value of water or sewage should be detd. in addn. to the KMnO₄ O consumed test. Investigations indi-

cated (1) Javelle water (NaOCl) is preferable to the $\text{Ca}(\text{OCl})_2$; (2) the detn. of the Br-combining value is superfluous; (3) in slightly polluted waters the Cl value is of more significance than the O consumed test.

F. W. MOHLMAN

Purification of sewage by the activated sludge process. REG. J. MORRIS. *S. African J. Sci.* 18, 215-23(1922).—The history of the process is reviewed, together with descriptions of English plants. Operating results with different types of aerators are included. M. recommends the process for large inland towns in tropical countries where drying of the sludge can be accomplished more easily, and the N conserved for fertilizers.

G. C. BAKER

Progress in the development of the activated sludge process. J. GARFIELD. *Surveyor* 62, 357-8(1922).—At Bury and Bradford tests have indicated that circulation alone is not sufficient to support oxidation unless the surface is broken up into spray. Fe has been removed from the Bradford sewage by cultivation of a coagulating organism and subsequent aeration. Dried sewage sludge (extd. settling tank sludge) has been sold at Bradford for as much as \$15 per ton, but there is no market at present.

F. W. MOHLMAN

Horsepower of activated sludge plants. *Surveyor* 62, 337(1922).—Diffused air at the Davyhulme plant at Manchester requires 35 h. p. per million gals., at 50% compressor efficiency. Mech. agitation at Sheffield is reported as requiring 32 h. p. per million gals. The sewage at Manchester is very oily and is not settled. The Sheffield sewage is settled six hours before circulation. Both methods should be compared under controlled identical conditions.

F. W. MOHLMAN

Decatur, Ill., builds modern sewage treatment plant. R. F. IMLER. *Eng. World* 21, 355-9, 374-7(1922); *Pub. Health Eng. Absts.* Feb. 3, 1923.—The plant comprises an overflow chamber and bypass around the plant to the Sangamon river, a grit chamber, $75' \times 10' \times 26'$, 6 primary settling tanks $27.83' \times 96'$, 16 sludge beds $25' \times 100'$, bypass from primary settling tanks around the filters, two sprinkling filters each $1\frac{1}{2}$ acres in size, and one secondary settling tank. Provisions are made for future additions to the plant.

G. C. BAKER

Dunstable sewage disposal works. W. F. WILKINS. *Surveyor* 62, 179(1922).—The flow from 20,000 people is passed through coarse screens, detritus and sedimentation tanks, and filtered through 9 ft. of graded gas clinkers. The effluent is used for irrigating a 31-acre farm.

F. W. MOHLMAN

Sewage treatment at Manchester. F. J. WEST. *Surveyor* 62, 309-12(1922).—See *C. A.* 17, 320.

F. W. MOHLMAN

The utilization of sewage in agriculture. E. KRÜGER. *Technik Landwirtschaft* 2, 38-40(1921); *Wasser u. Abwasser* 17, 283(1922).—In broad irrigation 1 acre will safely take care of the sewage of 100 people. The sewage farms of Berlin receive $14,000 \text{ m.}^3$ (3,700,000 gals.) per acre per year.

F. W. MOHLMAN

Measuring corrosion in water (SPELLER, KENDALL) 9. Corrosion of iron and steel in natural waters (WILSON) 9. Damage from O in boiler feed water (GIBSON) 9. Alcohol from garbage (U. S. pat. 1,440,727) 16.

FYFE, W. WALKER: *Automatic Pumping and Notes on Water Analysis and Filtration.* Edited by J. W. Fyfe. London: Charles Griffin & Co., Ltd. 112 pp. 7s. 6d. Reviewed in *Water & Water Eng.* 24, 460(1922).

KINNICUT, LEONARD P., WINSLOW, C.-E. A. AND PRATT, R. WINTHROP: *Sewage Disposal.* 2nd Ed. revised and enlarged. New York: John Wiley & Sons, Inc. 547 pp. \$5.00(25s.).

RACE, JOSEPH: *Chlorination of Water*. New York: John Wiley & Sons, Inc. 158 pp. \$1.50 (7s. 6d.).

Purifying water. J. R. McDERMET. U. S. 1,442,348, Jan. 16. After passing water through a zeolite filter it is introduced into an evaporator which is maintained under sufficiently low pressure to remove entrained air or other gases.

Purifying water for steam boilers. J. D. REEKIE and G. M. CROSSEN. U. S. 1,440,103, Dec. 26. Feed water is heated in a sep. vessel within the boiler before it mixes with the main body of water in the boiler and oil and mineral ppt. are sepd.

Treating liquids with chlorine. W. PATERSON. Brit. 188,045, July 28, 1921. In app. for *sterilizing or purifying* H_2O or other liquid by treatment with Cl of the type in which the flow of Cl is measured by taking the difference in the pressures on opposite sides of a restricted orifice, a seal of liquid not affecting or affected by the Cl is provided between the Cl control app. and the liquid to be treated. Cf. 158,578 (C. A. 15, 1958) and 166,191 (C. A. 16, 307).

Softening water; preventing and removing incrustation. L. F. C. M. VAN WEDDINGEN. Brit. 187,647, March 27, 1922. A reagent for softening feed water and preventing and removing incrustation in boilers is obtained by satg. a soln. of Na_2CO_3 at a temp. of 5° to 10° with aluminate and $Ba(OH)_2$ and adding ext. of tannin.

Precipitation chambers for purifying water. J. T. TRAVERS. U. S. 1,440,254, Dec. 26.

Apparatus for treating water with purifying chemicals and for sedimentation. W. R. MATHIS. U. S. 1,441,731, Jan. 9. The app. is adapted for treating H_2O with a coagulant and for sepg. and drying the resulting ppt. for regeneration of the reagent (by H_2SO_4 if $Al_2(SO_4)_3$ is used).

Ozone generator for water purifying apparatus. C. L. FITZ. U. S. 1,441,076, Jan. 2.

Apparatus for evaporating sea water. C. W. DYSON and M. C. STUART. U. S. 1,440,723, Jan. 2.

Filter for connection with water pipe systems. G. KNEUPER. U. S. 1,439,706, Dec. 26.

Purifying sewage or other polluted liquids. J. T. TRAVERS. U. S. 1,440,253, Dec. 26. Marl clay, lime and $FeSO_4$ are added as purifying reagents.

Fertilizers. E. H. SAMS. Brit. 187,423, Sept. 14, 1921. House refuse or sewage sludge is sprayed with ammoniacal liquid from gas works and then ground. Preparatory treatment of house refuse may include sorting or screening and grinding. Sewage sludge may be previously dried and crushed. Cf. C. A. 16, 135.

Purifying air. A. B. LAMB. U. S. 1,442,619, Jan. 16. Suspended matter is pptd. and air sterilized by elec. discharges and the treated air is then subjected to the action of absorbent or adsorbent material, to remove dust, smoke, bacteria and other impurities.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Biochemical problems in agriculture as related to food. W. H. HILL. *Sci. Agr.* 3, 105-9(1922).—A general discussion. J. J. SKINNER

Biochemical problems in agriculture with special reference to fruits. A. F. BARSS. *Sci. Agr.* 3, 100-4(1922).—A general discussion. J. J. SKINNER

Soil acidity—its nature, measurement and relation to plant distribution. E. T. WHERRY. *Smithsonian Rept.* 1920, 247-68(1922).—A summary of previous work

(*C. A.* 14, 1843, 1866, 2505, 2944; 15, 285) with some new data as to soil preference of individual plant species.

R. T. W.

Report, Division of Soils. F. J. SIEVERS. Washington Agr. Expt. Sta., *Bull.* 175, 40-4(1922).—*Soil nitrate studies.*—Past results have shown that when straw is plowed under immediately before seeding, available N is withdrawn from the soil, yields are reduced and a product of poor quality is obtained. Straw plowed under after summer fallow tillage also caused a depressing effect. The greatest reduction in nitrates and yield was obtained when straw was incorporated where the moisture content in the surface soil was lowest, with practically no reduction where surface moisture was maintained at a percentage optimum for nitrification. The bad effects of straw are more difficult to overcome in poorer soils. *Soil fertility problems in western Washington.*—The muck and peats of this section were found deficient in P and K. The least decomposed soils are the more deficient. The sands and sandy loams of the higher elevation are deficient in all fertilizer elements especially N. *Arid soil investigations.*—The variations in pptn. had very little effect on the amt. of Ca, K and P present in the soil. There was a direct variation in the amt. of N and C in that these elements increased with the pptn. The ratio was 1 to 12. The vegetable matter in arid soils is thought to have a higher N content than that of soils of regions of heavy pptn. *Magnesium carbonate injury.*—MgO emitted as a dust from a magnesite roaster and distributed through the air was deposited on surrounding agr. land and changed to $MgCO_3$. It produced alkali conditions in the soil and caused a bad physical condition, which prevented young plants from penetrating the crust. A toxic effect was produced which prevented the development of plants. An area of 1.5 miles was affected.

J. J. SKINNER

The adsorption processes in soils. D. J. HISSINK. *Intern. Mitt. Bodenk.* 12, 81-172(1922).—An exhaustive study is made of the bases present in soils with special reference to those replaceable by neutral salt solns. and those sol. in strong acids. The exchangeable bases are considered as being on the surface of the particles of clay and of the humus complex in an adsorbed condition. They are thought, however, to be held in ion form by chem. attraction. On the surface of the adsorbing clay and humus an elec. double layer is formed with the anion on the particle side and cation on the soln. side. The cations are principally of Na and K, the Ca and Mg compds. being but little ionized. Soil acids are found on the surface of adsorptively unsatd. soil particles. Former methods do not give an accurate measure of the exchangeable bases. A method is developed by which it is possible to sep. the bases exchangeable by neutral salts, the acid-sol. bases and $CaCO_3$. The method is as follows: Treat 25 g. of soil with 100 cc. of N NaCl soln., heat to 80 or 90°, shake, and allow to stand overnight. Then filter into a 1. flask and wash with N NaCl soln. When 1 l. has filtered through remove the funnel to another 1. flask and continue the washing until this is filled. Ca and Mg are then detd. in both flasks and the difference in the content of the 2 is taken as the exchangeable Ca and Mg. The exchangeable Na and K are obtained in a similar manner by treating with NH_4Cl soln. It is assumed that if $CaCO_3$ is present the same amt. will be dissolved in the 2nd l. as in the first; hence the difference represents only exchangeable bases. Acid-sol. bases are detd. by treatment with strong HCl. The investigation of a large number of soils indicates that in clay soils there is a very low content of acid-sol. Ca and Na. The avs. are 0.27 and 0.25%, resp., while the K and Mg are 1.34 and 0.826%, resp. Humus soils contain the largest amt. of their bases in exchangeable form, while soils which are composed mostly of weathered minerals are largely of the acid-sol. nature.

M. S. ANDERSON

Factors influencing the determination of sulfates in soil. C. T. HIRST and J. E. GREAVES. *Soil Science* 13, 231-49(1922).—A comparison is made of the recovery of SO_4 from H_2SO_4 solns. varying in concn. from 2 N to 0.1 N by the $BaSO_4$ gravimetric

method and the chromate volumetric method. At normal concn. concordant results were obtained but with the 0.1 N soln. only 89% was recovered by the chromate method. When the methods are compared on soil solns. extd. from soils by shaking with 5 parts H_2O to 1 part soil and filtering through a Pasteur-Chamberland filter, an av. of 96.7% SO_4 was recovered by the chromate method on the basis of 100% recovery by the $BaSO_4$ gravimetric method. Because of the greater rapidity of the volumetric method it is to be recommended where a large number of sulfate detns. are to be made. A correction can be applied depending upon the type of soil and the quantity of sulfates present. An extensive bibliography is given.

RICHARD BRADFELD

Effect of tree products on bacteriological activities in soil. I. Ammonification and nitrification. W. M. GIBBS AND C. H. WERKMAN. *Soil Science* 13, 303-22(1922).—Crop yields on the Helmer silt loam, a forest soil of Northern Idaho, decrease for the first 3 or 4 yrs. after clearing, then better crops are obtained. These soils are known as "turpentine" soils because it is thought that the substances detrimental to plant growth are forest by-products. A soil of low fertility, one of av. fertility and a garden soil of high fertility were treated with various forest by-products, sawdust from different trees, leaves, bark, "forest-floor," etc. All treatments retarded both ammonification and nitrification. Cedar sawdust was the most inhibitory, reducing ammonification 78.9%, white pine was least with 13.1%. $CaCO_3$ did not overcome this toxic action. Denitrification expts. indicated that the decrease of nitrate formation was due not to the denitrifying group but to inhibition of nitrifiers.

R. BRADFELD

The influence of moisture and soluble salts on the bacterial activities of the soil. J. E. GRAVES AND E. G. CARTER. *Soil Science* 13, 251-70(1922); cf. *C. A.* 16, 1477.—The influence of the Cl , NO_3 , SO_4 and CO_3 salts of Na, K, Mg and Ca upon the moisture requirements of a highly calcareous soil for ammonification and nitrification was detd. Untreated soil, that receiving Na_2CO_3 , K_2CO_3 , KNO_3 , $CaCO_3$, $CaSO_4$, $Ca(NO_3)_2$, $MgCl_2$ and $MgCO_3$, had a max. ammonifying power at a soil moisture content of 30%; with Na_2SO_4 , $NaNO_3$, KCl and K_2SO_4 the max. was at 35% H_2O ; while with $MgSO_4$ and $Mg(NO_3)_2$ it was at 25% H_2O . The relative toxicity of $NaCl$, Na_2CO_3 , K_2CO_3 and $CaCO_3$ was decreased with an increased H_2O content, indicating that the toxic influence might be due to the high osmotic pressure. All other salts became relatively more toxic, indicating some physiologic effect upon the organisms. With the nitrifying organisms, untreated soil and those treated with KCl , K_2CO_3 , K_2SO_4 , KNO_3 , $MgCl_2$ and $MgCO_3$ show a max. nitrification at H_2O contents of 20% compared with $CaCO_3$, $Mg(NO_3)_2$, $MgSO_4$ at 25% and $NaCl$ and $CaCl_2$ at 30%. The relative toxicity of all salts to the nitrifying organism decreased as the H_2O content increased. Mere changing of H_2O content with a soil contg. small quantities of KCl , K_2SO_4 , $Mg(NO_3)_2$ and $MgCl_2$ transformed it from a toxic to a strongly stimulating medium for nitrifiers.

R. BRADFELD

The effect of reaction on the fixation of nitrogen by Azotobacter. H. W. JOHNSON AND C. B. LIPMAN. *Univ. California Pub. Agr. Sci.* 4, 397-405(1922).—A vigorous strain of *Azotobacter chroococcum* was grown in solns. whose reactions were definitely detd. by the hydrogen electrode. The N fixed in the soln. of each reaction was detd. and the changes in reaction during incubation were measured. The reaction of the soln. below pH 8.0 changed very little, because below pH 6.0 no growth occurred, and between 6.0 and 8.0 the soln. was highly buffered. Above pH 8.0 the reaction changed greatly, possibly because of incomplete reaction of the alkali at the time of titration, but more probably because of absorption of CO_2 by the strong alkali. The amt. of N fixed was not greatly affected by reactions between pH values of 6.2 and 8.8, although reactions around pH 7.0 and 8.0 seemed to be most favorable. Slight changes outside of these values caused an abrupt decrease in fixation.

J. J. SKINNER

Soil reaction, water snails and liver flukes. W. R. G. ATKINS AND M. V. LEBOUR.

Nature 111, 83(1923).—The distribution of snail species becomes limited in the more acid habitats. Over quartzite at p_H 4.8 a few Hyatinias are all that could be found, whereas around p_H 7 numerous species exist. Fewer species are found at p_H 8, but those that are found are often in great numbers, such as *Helicella caperata* and more especially *H. virgata*. Upland peat soil is usually around p_H 4.6, and rough pastures may be between that and p_H 5.4 or something over, so it seems highly probable that liming such land, by bringing it to the neighborhood of p_H 7, does make the conditions more favorable for the snails concerned in the transmission of disease. Wallace, *Nature* 110, 845(1922), directs attention to the prevalence of liver fluke disease in the Swansea valley, where rough pastures have been limed.

BENJAMIN HARROW

Origin of the "Molken" soils. O. VON LINSTOW. *Intern. Mitt. Bodenk.* 12, 178-9 (1922).—Chem. analyses of 14 "Molken" soils of different textures are given. The differences in compn. are discussed with respect to the geological processes involved in their formation.

M. S. ANDERSON

Composition of the soils of Bell, Jefferson, Smith, Taylor, and Webb counties. G. S. FRAPS. Texas Agr. Expt. Sta., *Bull.* 301, 66 pp.(1922).—Deals with the chem. compn. of samples of typical soils from 5 counties of Texas.

J. J. SKINNER

Alkali soils containing alum in the humid region of Finland. B. AARNIO. *Intern. Mitt. Bodenk.* 12, 180-85(1922).—In certain regions of Finland having an annual rainfall of 500-650 mm. sol. Al salts are concd. at the soil surface. Samples from the upper 10 cm. contain 0.30-2.45% sol. salts. The salts consist chiefly of Al_2O_3 , CaO , Na_2O and SO_2 . The Al_2O_3 content varies from 2.28 to 10.77%. These soils are strongly acid, having H-ion concn. in the surface layer of 1.3×10^{-4} — 2.21×10^{-3} . Acidity and salt content are too strong for plant growth.

M. S. ANDERSON

Influence of soil colloids on availability of salts. N. E. GORDON AND E. B. STARKEY. *Soil Science* 14, 1-7(1922).—The adsorption of KNO_3 , K_2SO_4 , $Ca(NO_3)_2$, $CaSO_4$, $CaH_2(PO_4)_2$, $Mg(NO_3)_2$, $MgSO_4$ and $MgH_2(PO_4)_2$ by pure hydrogels of silica, alumina and iron was studied by detg. the change in concn. of 0.05 *N* solns. of the salts after shaking with weighed quantities of the gels until equil. was established. The p_H of the solns. varied by adding NaOH or HCl. Both ions of $CaH_2(PO_4)_2$ were highly adsorbed by alumina and iron but very slightly by silica. All gels adsorbed more Ca from the more alk. solns. K was more highly adsorbed by silica than Ca. Very slight changes in p_H around the neutral point caused very large changes in the amt. of K adsorbed.

R. BRADFIELD

The value of "Rhenania" phosphate. A. GEHRING. *Zentr. Kundung. Ind.* 27, 1-2(1922); *Chimie et industrie* 8, 1310(1922).—"Rhenania" phosphate is obtained by heating to redness a mixt. of natural phosphate, phonolite, and lime, with a certain amt. of basic substances. It averages about 12% P_2O_5 , of which 75% is sol. in 2% citric acid. Pot. expts. by Remy and Meiske showed that in half the tests the citric sol. P_2O_5 of the Rhenania was equal to that of basic slag, while in the remaining half it was superior. The results are affected to a considerable extent by the nature and reaction of the soil. Tacke published results obtained in field expts. In slightly acid soils Rhenania phosphate is equiv. to basic slag, but in soils which are not acid the former is decidedly inferior. Nolts, exptg. with sugar beets in a neutral soil, concludes that Rhenania and basic slag give the same yield and the same net profit.

A. P.-C.

Forest fertilizer experiments in the government district of Sigmarin. LENT. *Mitt. deut. Landw.-ges.* 37, 663-6(1922).—A summary of 15 yrs.' fertilizer expts. on pine trees. Applications of P_2O_5 and K_2O gave slightly better results than P_2O_5 alone, the latter being 100 as compared to 70 for the check plots, on the basis of the height of the trees. $CaCO_3$ and $(NH_4)_2SO_4$ were ineffective and in many cases gave lower results than the checks." Plowing and growing clover in connection with the fertilizer treatments gave

better results than the corresponding plots receiving only fertilizers.

K. D. JACOB

Sulfur as a plant food. J. L. SR. JOHN. Report Division of Chemistry, Washington Agr. Expt. Sta., *Bull.* 175, 15-16(1922).—An application of elemental S at the rate of 160 and 500 lbs. per acre causes an accumulation of soil NO_3 while a 1000 lbs. application causes a decrease. Nitrate accumulation was decreased by the use of S on manured soils. S was oxidized fairly rapidly in the soils tested and the rate of oxidation was affected but little by the addition of manure. The rate of oxidation of S applied at the rate of 500 lb. per acre seems to be about the same in Palouse and Lind soils. Palouse soil seems to contain more sol. sulfate than Lind soil.

J. J. SKINNER

Value of waste-lime from cellulose factories as soil amendment. HJ. VON FEILITZEN. *Kgl. Landbruks-Akad. Handl. o. Tid.* 61, 567-87(1922).—The waste lime from the 26 cellulose factories of Sweden is equiv. to 54,000 tons CaO per year. Pot tests with barley and white mustard showed that this waste lime has the same value for acid soil as hydrated lime. No harmful effects were observed from its use. C. O. SWANSON

The importance of chemical fertilizers in sugar cane culture. P. DE SORNAY. *Rev. agr. Maurice* 1, 173-8(1922).—This is a general discussion with special reference to Mauritius conditions. There is a tendency to use too much N and not enough P and K.

F. W. Z.

The use of molasses as fertilizer. L. FAUQUE. *Rev. agr. Maurice* 1, 179-82(1922).—Molasses is an excellent fertilizer; it adds plant food directly, makes more available from the soil, and favors the development of *Azotobacter*. But its action is slow, because, as shown by lysimeter tests, it retards nitrification and increases denitrification. Addn. of lime and thorough aeration counteract this effect. In order to obtain the best results it is necessary to make applications early, to lime the land and cultivate it well.

F. W. ZERBAN

Use of molasses as fertilizer in Mauritius. P. DE SORNAY. *Rev. agr. Maurice* 1, 229-40(1922); cf. preceding abstr.—There are 2 theories regarding the cause of the excellent results obtained in Mauritius, one ascribing them principally to biol. action favoring the fixation of N from the air, the other explaining them by the K content of the molasses. De S. believes that the former theory has not been proven by Fauque, on account of exptl. error. When molasses is applied to the soil, the sucrose disappears completely within a few days, and the reducing sugars within 2 weeks. It is believed that this fermentation process produces chem. changes in the soil, making plant foods more available. Results of expts. seem to confirm this. The K_2O in the molasses may serve as a neutralizing agent in the process. The effect of molasses varies with its compn. and with local conditions, as shown by tests made in different countries, but an injurious action has not been proven. The molasses may be applied as such, or diluted with water, or mixed with filter press cake and bagasse ash. Numerous field tests in Mauritius, which are given in tabular form, have given increases of from 0.5 to over 8 tons of cane per acre. The best results are obtained with plant cane, and in connection with chem. fertilizers.

F. W. ZERBAN

Nitrification of filter press cake in the acid red clay soils of Porto Rico. J. H. RAMIREZ. *Louisiana Planter* 70, 48-50(1923).—Filter press cake contains on a water-free basis N 2.14, P_2O_5 2.74, CaO 3.11, K_2O 0.46% and is perhaps richer in plant food than stable manure. 15-25 tons of press cake per acre gave the best results. The increase in nitric N began the third month after application. A small loss by denitrification occurred.

C. H. CHRISTMAN

The conservation of litter straw. NOLTE. *Mitt. deut. Landw.-ges.* 37, No. 47, 1-2(1922).—The value of peat, forest moss, and fern litter, pine twigs, soil, water grass,

saw dust, and tan bark for litter is discussed, and their absorptive powers, N, P_2O_5 , K_2O and Ca content are given. K. D. JACOB

Biochemical aspects of insect control. R. C. TREHERNE. *Sci. Agr.* 3, 109-13 (1922).—A general discussion. J. J. SKINNER

The oleoresin of pyrethrum. R. M. GATTEFOSSÉ. *Rev. vit.* 58, 11-3 (1923).—A discussion. P. R. DAWSON

Protection against infection of vineyards by insecticidal and fungicidal lime-sulfur sprays. ABEL BECKERICH. *Prog. agr. vit.* 78, 522-6; *Rev. vit.* 57, 341-6 (1922).—A review and discussion of the economic, chem. and practical considerations involved in the theory and practice of sulfide sprays. P. R. DAWSON

Spray poisoning of bees. A. L. MELANDER. Wash. Agr. Expt. Sta., *Bull.* 175, 24 (1922).—Dormant sol-Oil, Milkol, creasol, nicotine sulfate, butyric acid, and crude pyroigneous acid were tried in orchard sprays as bee repellents. Their degree of effectiveness was in the order given. Bees ceased frequenting alfalfa cover crop immediately after nicotine sulfate was added to arsenical sprays applied to orchard. J. J. SKINNER

Carbon disulfide as an insecticide. PIERRE LARUE. *Rev. vit.* 56, 223-6 (1922).—A review of the properties of CS_2 and its uses as an agricultural disinfectant. P. R. DAWSON

Phosphoric acid in cane juices (WALKER) 28. Utilization of sewage in agriculture (KRÜGER) 14. Fertilizers (Brit. pat. 187,423) 14.

AGREBOE, FR.: *Neue Düngewirtschaft ohne Auslandsphosphate*. Berlin: P. Parey. 52 pp. M 15.

HEINRICH, REINHOLD: *Dünger und Düngen*. 8th Rev. ed. Edited by Nolte and Heinrich. Berlin: P. Parey. 174 pp. M 38.

MEYER, LOTHAR: *Neuzeitliche Stickstoffdüngung*. Neudamm: J. Neumann. 51 pp. M 10.

SCHIEFFER, FRANZ ANTON: *Leitfaden der Chemie für Landwirte*. Hanover: M. & H. Schaper. 189 pp. M 31.

Fertilizer. J. L. STOLTZ. U. S. 1,442,239, Jan. 16. Humus-contg. material and nitrifying bacteria are incorporated with a mixt. of $CaCO_3$ and phosphate rock in finely divided state.

Fertilizer. K. P. McELROY. U. S. 1,441,694, Jan. 9. Air is blown into a charge of ignited fuel, alkali and Fe to form a fume comprising cyanide which is condensed and digested with acid or acid phosphate to form a fertilizer.

Fertilizer. E. A. MORGAN. U. S. 1,440,836, Jan. 2. A com. fertilizer is formed of hard-wood ashes 6, crude K_2CO_3 2, S 2, $NaNO_3$ 4, ground bone 3 and acid phosphate 3 parts.

Fertilizer stock from fish. A. EHRENBREICH and A. ROGERS. U. S. 1,441,219, Jan. 9. Raw fish is disintegrated, sprinkled with concd. H_2SO_4 to prevent loss of NH_3 and then dried.

Fertilizers; ammonium salts; ammonia. E. L. PEASE. Brit. 187,251, April 15, 1921. Fertilizers contg. an NH_4 compd. or compds. and a secondary fertilizing agent or agents, such as a salt of K or a phosphate, are obtained by reaction between gases contg. NH_3 and the semi-dry product obtained by treating with acid a naturally occurring material that contains the secondary fertilizing agent or agents, but which is free, or almost free, from lime and is not generally regarded as a fertilizer in itself. Thus clay contg. a compd. of K may be treated with H_2SO_4 , if desired after drying and pul-

verizing, in sufficient amt. to constitute a semi-dry mass, which is brought into contact with gases contg. NH_3 .

Guanidine salts. J. S. BLAIR and J. M. BRAHAM. U. S. 1,441,206, Jan. 9. "Lime-nitrogen" is extd. with H_2O , the ext. is filtered and neutralized with an inorg. acid, preferably H_2SO_4 . Pptd. CaSO_4 is filtered out and the filtrate obtained is heated in an autoclave to 150 – 180° with NH_4NO_3 in excess of equi-mol. proportion in order to produce *guanidine nitrate*. Other guanidine salts may be obtained from corresponding NH_4 salts.

Guanidine nitrate. T. L. DAVIS. U. S. 1,440,063, Dec. 26. Guanidine nitrate is prepd. by heating a mixt. of dicyanodiamide with at least 2 mol. proportions of NH_4NO_3 and H_2O . Cf. C. A. 16, 410.

Urea phosphate. F. CLARKSON and J. M. BRAHAM. U. S. 1,440,056, Dec. 26. H_3PO_4 of at least 55% concn. and urea are brought together in substantially equimol. proportions.

16—THE FERMENTATION INDUSTRIES

C. N. FREY

Estimation by the hydrogen ion method of organic acids and their compounds in wine. C. VON DER HEIDE and W. J. BARAGIOLA. *Z. anal. Chem.* 62, 34 48(1923).—The authors show by means of a correction value which they apply that previous results for the cstn. of these acids do not approach theoretical accuracy close enough to be any longer satisfactory. They further demonstrate that the org. acids can be arranged on a basis of their dissociation constns. and they call especial attention to the 2 dissociation constns. of dibasic acids. Cf. C. A. 5, 2297, 3316. T. SWANN HARDING

A report on the manufacture of industrial alcohol from Hawaiian molasses. W. L. MCCLEERY and H. P. AGEE. *Louisiana Planter* 69, 449–50, 468–70, 487–90(1922).—The cost of producing industrial alc., exclusive of the molasses, is 8–11 c. per gallon. In stoves 1.75 times as much alc. is required as kerosene and in motors 1.4 times as much as gasoline. The formula, 90–92% EtOH 100 gals., ether 30 gals., kerosene 2 gals., and pyridine or aniline 1 gal., is best for motor alc. A paraffin-base oil is used in motors and carburetors equipped with metal floats have proved to be the best. The thermal value of alc. to kerosene is 1.795 and to gasoline 1.57. Estimates are given in detail for the cost of erecting and operating a plant having a capacity of 1000 gals. of motor alc. daily. C. H. CHRISTMAN

Yeast growth. LEWIS EYNON. *J. Soc. Chem. Ind.* 40, 187–8R(1921).—A discussion of the work of Slaton (cf. C. A. 13, 1480; 15, 1552) in relation to that of Pasteur, and their interpretations of certain phenomena. C. C. DAVIS

The manufacture of sodium cyanide from distillery and sugar-house residues (DEJUSSIEU) 28.

Dealcoholized beverage. H. HEUSER. U. S. 1,441,726, Jan. 9. In dealcoholizing beverages such as beer by heating, pepsin is added to convert into sol. form the nitrogenous compds. coagulable during the dealcoholization.

Alcohol from garbage. M. E. FAUST. U. S. 1,440,727, Jan. 2. Garbage is heated to evap. H_2O and effect dextrinization, some of the aq. vapor is condensed and it is subjected to alc. fermentation with distn. and recovery of the alc. formed.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

The new wound powder, "Albertan." F. BRÜNING. *Deut. med. Wochschr.* **48**, 622-3(1922).—Albertan is a compd. of Al with some phenol alcs. It is recommended as an iodoform substitute. S. AMBERG

A disinfecting and astringent mixture. E. EBELER. *Münch. med. Wochschr.* **68**, 1585(1921).—Al acetotartrate is finely powd. and mixed with Na perborate. A 15% soln. corresponds to a 3% H_2O_2 soln. S. AMBERG

Insulin and the steps taken to secure an effective preparation. J. J. R. MACLEOD. *Can. Med. Assoc. J.* **12**, 899-901(1922). A. T. CAMERON

Digest of comments on the Pharmacopeia of the United States of America and on The National Formulary for 1920. A. G. DuMEZ. U. S. Pub. Health Service, Hyg. Lab., *Bull.* **131**, 410 pp.(1922). E. J. C.

Determination of chloral hydrate. I. M. KOLTHOFF. *Pharm. Weekblad* **60**, 2-8(1923).—Two methods are described for detg. chloral hydrate in the com. product. (a) *Acidimetric method.*—Heat 10 cc. of a 0.1 *M* soln. of the substance with 5 cc. 4 *N* alkali and 15 cc. EtOH in a sealed tube at 90-100 for 2 hrs. with occasional shaking. Det. the Cl by the method of Volhard or that of Votocek. (b) *Iodometric method.*—To 25 cc. 0.1 *N* I add 10 cc. 2 *N* NaOH and 10 cc. of a 0.1 *N* soln. of the substance. Stopper the container and let stand 1 hr. Acidify with dil. HCl and titrate the excess I with $Na_2S_2O_3$. One cc. 0.1 *N* I = 8.27 mg. chloral hydrate. The reducing power of chloral hydrate is much greater in alk. than in acid medium. In the presence of acid Br does not oxidize chloral hydrate to CCl_3CO_2H . A. W. DOX

Iodometric titration of sublimate. I. M. KOLTHOFF. *Pharm. Weekblad* **60**, 18-20 (1923).—An improvement of the method of Kolthoff and Keyzer (*C. A.* **14**, 3035). To 10 cc. of 0.2 *N* soln. of $HgCl_2$ add 3 cc. of 3% H_2O_2 and 20 cc. of 0.2 *N* $Ba(OH)_2$ and carefully rotate the flask. Place for at least 10 min. on a boiling water bath, shaking repeatedly so that the HgO first formed is completely reduced to metallic Hg . Cool and add 25 cc. of 0.1 *N* I and shake 2 min. Acidify with 3 cc. of 4 *N* HCl and shake until all the Hg has dissolved. Titrate the excess I with $Na_2S_2O_3$. A. W. DOX

Processes and manipulations in the manufacture of perfumes and toilet waters. ANON. *Perfumery Essent. Oil Record* **13**, 417-8(1922).—A discussion of the operations of filtration and aging, odor and cosmetic incompatibilities, together with brief mention of the dyes and solvents commonly used. W. O. EMERY

Efficiency of some common anti-ferments. E. H. HARVEY. *Am. J. Pharm.* **94**, 797-801(1922).—A method is described for measuring the retarding action of various anti-ferments on yeast-sucrose solns. The data may be interpreted as a measure of the efficiency of the several materials commonly used for preventing fermentation. While ultra-violet radiation is largely used at present as a bactericide it would seem that for certain purposes its use might be further extended as an anti-ferment, especially since no toxic residue is left in the treated material. In most cases the action of the anti-ferment is one of gradual retardation rather than immediate cessation of activity. A number of commonly used materials have a low percentage of efficiency.

Analysis of a few official tablets. MAURICE FRANÇOIS. *Ann. Jals.* **15**, 470-9 (1922).—*Detection of gum tragacanth.*—To 1 tablet in a test-tube add 10 cc. of cold water, let stand 48 hrs. If the tablet was prepd. with gum tragacanth there will remain a gelatinous, opaline mass, which roughly retains the shape of the tablet. *Detection of gum arabic.*—Treat 20 tablets with 40 cc., of cold water for 48 hrs., filter (generally requires several days) in a covered funnel, add 5 vol. of 95% alc. to the filtrate, decant the super-

W. G. GAESSLER

nantant liquid after some hrs., dissolve the residue in a few cc. of water and reprecipitate with alc. Filter, air-dry at room temp., prep. a 1% soln. of the gum. The polarization in a 2-dm. tube should be $-1^{\circ} 4'$; gives a white ppt. with Pb subacetate, and a white gelatinous ppt. with Fehling soln., but does not reduce the latter on boiling. On boiling with H_2SO_4 it is hydrolyzed to reducing sugars. Heating the dry powder with concd. HCl over a naked flame gives furfural. *Detection of carmine*.—Treat 1 tablet with 10 cc. of cold water for 24 hrs., filter, ext. the carmine by repeatedly passing through the filter a mixt. of 10 drops of NH_4OH and 20 drops of water, shake the soln. with 5 cc. of Am alc., which should remain uncolored. On acidifying with AcOH and again shaking the Am alc. remains uncolored; but on acidifying with HCl and shaking the Am alc. turns red. Draw off the Am alc., add 1 cc. of water, and a slight excess of U acetate; the Am alc. is decolorized and the water turns green. *KClO_3 tablets*.—Treat 1 tablet with 10 cc. of water for 24–48 hrs. and filter. Test the filtrate by means of $\text{C}_6\text{H}_5\text{NH}_2$ and H_2SO_4 (intense, but fugitive, blue color), indigo sulfate (not decolorized until addition of Na_2SO_3), and AgNO_3 (pptn. only after reduction to chloride). The KClO_3 can be detd. by carefully igniting to a white ash, taking the usual precautions to avoid loss. A mixt. of 0.200 g. KClO_3 , 0.100 g. gum tragacanth and 2 g. of sugar gave 0.121 g. ash = 0.199 g. KClO_3 . *Borax tablets*.—Careful ashing (charring, extg. with water, filtering, etc.) with subsequent dehydration at 300° gives $\text{Na}_2\text{B}_4\text{O}_7$, which is identified by making a bead and then adding a trace of Co salt (blue); or by making into a paste with CaF_2 and H_2SO_4 and making a flame test (intense green). A mixt. of 0.500 g. of borax, 0.100 g. of gum tragacanth, and 5 g. of sugar gave 0.260 g. ash = 0.490 g. borax. *NaHCO_3 tablets*.—Ignite to a white ash (with usual precautions), and det. the purity of the NaHCO_3 by testing for chlorides and sulfates, and by detg. the alk. of the ash. *S tablets*.—Treat 2 tablets for 24 hrs. with 40 cc. of water, add 40 drops of concd. HCl , heat 1 hr. on the water bath, filter on tared filters, and weigh the S, which is identified by burning, melting, distg., and formation of Na_2S_x . *Santonin tablets*.—Mix thoroughly 10 finely ground tablets with 10 g. of $\text{Ca}(\text{OH})_2$, transfer to a 125-cc. Erlenmeyer flask, add 50 cc. of 95% alc., heat on the water bath under a reflux condenser for 1 hr. (keeping just below the b. p.), decant through a large plain filter into a 500-cc. flask, repeat the digestion 3 times, add 100 cc. of water to the filtrate, distil over a naked flame till 180–190 cc. have passed over, acidify the residue with 10 drops of HCl , ext. with 6 20-cc. portions of CHCl_3 , wash the combined CHCl_3 exts. once with 20 cc. of water, filter into a large crystg. dish, and allow to evap. spontaneously in the dark. Weigh as santonin. Identify as follows: about 1 mg. examd. microscopically should appear as plainly striated, rectangular, tabular crystals. Cover with some powdered KOH (about the size of wheat grain), heat over a very small flame until the KOH is just fused, when there should be carmine striations, which under the microscope are seen to consist of colored but undissolved santonin crystals. On treating with 95% alc., the latter is colored red. A mixt. of 0.100 g. of santonin, 0.200 g. of gum tragacanth, and 10 g. of sugar gave 0.0995 g. of santonin, which was very pure. *Chocolate and santonin tablets*. The method is essentially the same as above. As the alc. exts. some of the cacao fat, it must be eliminated after distn. by thorough cooling of the residue and subsequent filtration. A mixt. of 0.100 g. of santonin and 10 g. of chocolate gave 0.102 g. of santonin.

A. P.-C.

Italian camphor. V. MASSERA. *Riv. ital. ess. prof.* 4, 63–4 (1922); *Chimie et industrie* 8, 1289 (1922).—Steam distn. in a 200-l. still (40 kg. of material and 40 l. of water) gave a 1.2% yield of camphor, and 0.3% of an essential oil with the following consts.: d_{20}^{20} 0.922, $[\alpha]_D^{20}$ 37° , n_D^{20} 1.4768, acid no. 1.06, sapon. no. 4.26, sapon. no. after acetylation 24.52. It is not completely sol. in 80% alc., but miscible in all proportions with 90% alc.

A. P.-C.

Essential oils from uncultivated plants in Calabria. F. LAFACE. *Riv. ital. ess. prof.* 4, 64-7(1922); *Chimie et industrie* 8, 1289(1922).—Oil of *Calamintha nepeta*, Sawi., is pale yellow with a penetrating odor similar to that of pulegone. Yield 1.88%. d_{15} 0.9350, $[\alpha]_D^{20} + 16^\circ$, acid no. 0.56, sapon. no. 11.3, sapon. no. after acetylation 57.87, total alc. (as menthol) 16.12%, n_D^{20} 1.4584, sol. in 2 vol. of 70% alc. Oil of *Mentha pulegium* L. is light yellow with a penetrating odor. Yield 1.75%. Sp. gr. 0.931, $[\alpha] + 33^\circ$, n 1.4805, sapon. no. 7.47, sapon. no. after acetylation 33.6, sol. in 1.7 vol. of 70% alc., contains 52% of pulegone and a small amt. of another ketone, probably menthone. Oil of wild marjoram is obtained in 0.35% yield, has an intense yellow color and a strong odor of camphor. Sp. gr. 0.918, $[\alpha] - 1^\circ 40'$, n 1.4991, sol. in 2 vol. of 80% alc. Oil of arborescent mugwort (*Artemisia*), is intensely blue, so that $[\alpha]$ and n could not be detd. It has an absinth-like odor. Yield 0.2%. Sp. gr. 0.943, acid no. 10.5, sapon. no. 24.83, sapon. no. after acetylation 47.6, total alc. (as $C_{10}H_{18}O$) 13.08%. Oil of *Mentha aquatica* L. is light yellow and has an agreeable odor like peppermint. Yield 0.03%. Sp. gr. 0.955, $[\alpha] + 44^\circ 36'$, n 1.4895, sapon. no. 72.8, sapon. no. after acetylation 87.73, acid no. 0.56, sol. in 0.6 vol. of 85% alc. Oil of rosemary.—Yield 0.22%. Sp. gr. 0.9173, $[\alpha] - 3^\circ 15'$, n 1.4680, acid no. 0.84, sapon. no. 7.4, sapon. no. after acetylation 30.05, total alc. (as borneol) 8.36%, sol. in 1.2 vol. of 80% alc. Oil of Mugwort (*Artemisia*) is brownish yellow with slight greenish fluorescence. Yield 0.32%. Sp. gr. 0.945, $[\alpha] - 8^\circ 12'$, acid no. 0.68, sapon. no. 7.47, sapon. no. after acetylation 32.66, sol. to a clear soln. in 9 vol. of 85% alc. Oil of *Inula helenium* L. is greenish yellow. Yield 0.2%. Sp. gr. 0.965, $[\alpha] - 28^\circ$, sapon. no. 154.93, sapon. no. after acetylation 263.2, acid no. 2.1, n 1.4790. A. P.-C.

The preparation of extractum fluidum chinæ and decoctum chinæ acidum. H. CEDERBERG. *Stenskt Farm. Tids.* 26, 447-50(1922).—The following procedure is given for the prepn. of extr. fl. chinæ: cortex (no. 30) 100 parts, HCl (dild.) 40 parts, glycerol 20 parts are mixed in a percolator and set aside overnight. Next day water is added and when the liquid begins to drip the percolator is cut off and let stand 48 hrs. It is then percolated until no positive test is given by Na_2CO_3 . The first 70 parts of the fluid is set aside and the following percolate is evapd. to a vol. corresponding to 20 parts. These are then added to the 70 parts and the whole is dild. to 100 parts with alc. The yield is about 85%. The most important detail in the extn. is to ascertain the amt. of HCl to add. ($\%$ alkaloid $\times 2.35$) + 3.25 gives the g. 10% HCl required. In estg. the alkaloid digest 2.5 g. bark in 5 g. 10% HCl and 17 g. H_2O 15 min. on a water bath and when cool shake with 50 g. Et_2O and 25 g. $CHCl_3$. Add NaOH soln. (5 g., concn. not stated) and shake vigorously for 10 min. Add 2 g. tragacanth powder, shake and strain through cotton. Distil 60 g. of the clear liquid, treat the residue with 3-5 cc. portions of Et_2O and evap. completely after each addition. Dissolve in 10 cc. abs. alc. dil. with 30 cc. H_2O and titrate with 0.1 N HCl, with methyl red as indicator.

A. R. ROSE

Apparatus for drying drugs, etc. (U. S. pat. 1,442,179) 1.

ARENDs, GHO.: Neue Arzneimittel und pharmazeutische Spezialitäten, einschliessl. d. neuen Drogen, Organ-u. Serumpräparate, mit zahlr. Vorschriften zu Ersatzmitteln u. e. Erklärung d. gebräuchlichsten med. Kunstausdrücke. 6th Rev. ed. Berlin: Julius Springer. 578 pp. M 66.

The Chemist and Druggist Diary, 1923. London: The Chemist and Druggist. 428 pp. Reviewed in *Pharm. J.* 110, 12(1923).

DUBOSC, A., AND TRABUT, L.: Le camphre et sa synthèse et la culture industrielle du camphrier. Lyon, 285 rue Jean-Jaurès: Pierre Argence. 64 pp. Fr. 6. Postage extra. Reviewed in *Am. Perfumer* 17, 510(1923).

FULLER, HENRY C.: *The Story of Drugs. A Popular Exposition of Their Origin, Preparation and Commercial Importance.* New York: Century. \$3. 358 pp.

GATTÉFOSSE, R. M.: *Formulary of the Parisian Perfumer.* 4th Ed. Villeur Bannelez-Lyon, France: Parfumerie Moderne, No. 112, Route de Crénieu. Reviewed in *Chem. News* 126, 36(1923).

GIOSIA, A.: *Chimica farmaceutica inorganica.* 2 Vol. Padua: La Litotipo. 242 pp. each. L. 17.50 and L. 35

THURSTON, AZOR: *Pharmaceutical and Food Analysis.* New York: D. Van Nostrand Co. 409 pp. \$4.50. Reviewed in *Am. J. Pharm.* 95, 60(1923).

Year Book of Pharmacy, 1922. Edited by J. O. Braithwaite and C. H. Hampshire. London: J. and A. Churchill. 546 pp. 12s. 6d. Reviewed in *Pharm. J.* 109, 508(1922).

Synthetic drugs. SOC. ANON. POUR L'IND. CHIM. À BÂLE. *Brit.* 187,129, Oct. 4, 1921. Optically active aromatic amino alcohols are obtained by reducing the corresponding amino ketone salts of optically active acids, sepg. the mixts. of isomerides so obtained, and liberating the free bases by alkali. Cf. *C. A.* 17, 326.

Synthetic drugs. L. CASSELLA & Co., GRS. *Brit.* 188,127, Sept. 1, 1921. Acridinium salts of fatty acids are prepd. by treating acridinium salts of mineral acids with salts of fatty acids of high mol. wt. Examples are given of 3,6-diamino-10-methylacridinium stearate, 2,7-dimethyl-3,6-diamino-10-methylacridinium stearate, and 3,6-diamino-10-methylacridinium palmitate. The products are sol. in fats and oils and suitable for therapeutic use.

Pharmaceutical compound of glutaminic acid and calcium bromide. R. BERENDES and W. GRÜTTEFIEN. U. S. 1,440,269, Dec. 26. A compd. which when dried at 90–100° is a whitish salt of neutral reaction and agreeable taste, sol. in H₂O and possessing sedative properties, is prepd. by evapg. the aq. soln. resulting from reaction of glutamic acid, CaCO₃, and CaBr₂ in H₂O.

Gelatin-hexamethylenetetraminediiodide. R. BENKÖ. U. S. 1,440,813, Jan. 2. A compd. readily sol. in H₂O and glycerol and forming a yellow ppt. with AgNO₃, and hexamethylenetetraminediiodide with H₂O₂, is prepd. by adding I to a soln. of gelatin and (CH₂)₆N₄, heating and evapg. *in vacuo*.

Sodium compounds of dihydroxydiaminoarsenobenzene. U. SUZUKI. U. S. 1,440,848–9–50, Jan. 2. NaOMe or NaOEt is added to a soln. of a hydrochloride of dihydroxydiaminoarsenobenzene in MeOH or EtOH, to form a Na compd. which is adapted for therapeutic use because of its low toxicity.

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

Fifty-eighth annual report of Alkali-Works' Inspector, 1921. T. L. BAILEY. *Gas J.* 159, 149–53; *Chem. Trade J.* 71, 69–71(1922). In regard to H₂SO₄ manuf. spent oxide is assuming greater importance as a source of S and several plants are installing app. for burning it. The advantage is that a practically non-arsenical acid is produced directly. The extension of this process emphasizes the need, however, for adopting the best possible means of dust deposition. The NH₃-oxidation method of providing N oxides for H₂SO₄ chambers has been still further established at several plants. By using a gas mixt. contg. 10% of NH₃, and maintaining a satisfactory gauze temp., excellent results are obtainable. Considerable advantage is gained by preheating the NH₃-air mixt. by some form of heat interchanger. A tendency to increased recovery of NH₄Cl at coke-oven works is recorded, and the advantages of a dry neutral sulfate for agr. pur-

poses are being more and more recognized and methods are being perfected for its production. Considerable difficulty was experienced in disposing of effluent liquors from NH_3 plants, the vol. of which depends upon the NH_3 content of the liquor distd., the amt. of steam used on the still and the vol. of lime water added to liberate the fixed NH_3 . On gas works the av. vol. per ton of sulfate made is about 4000 gal. for a gas liquor of 8-9 oz. strength; at coke-oven works using the old process the vol. would be more. The most noxious constituent is the phenols, which can largely be removed from soln. by steam treatment, but still leaving the liquor with its original color. To decolorize the liquor a proportion of mineral acid is added; about 4 lb. of 100% H_2SO_4 per 4000 gal. of liquor if the amt. of free lime is at a minimum. A practical method is suggested, and exptl. results are given, of deodorizing and decolorizing an effluent liquor by treatment with boiler flue gases and steam in a suitable scrubber. The final figures show a removal of 56% of the phenols, and 7.5% of the thiocyanate, and a reduction of the O absorbed of 31.5%.

J. L. WILBY

Sulfuric acid manufacture. The theory of the chamber process. C. IRWIN. *Chem. Age* (London) 7, 938(1922).—Lunge's theory is reviewed. I. has found that if the nitric acid is too weak (below 60%), which is being used on the Glover tower as the source of niter, the niter rate goes up. This agrees with theory. The investigation of lead, and its resistance to corrosion as affected by compn., is urged.

F. C. Z.

The production of nitrogen and hydrogen for synthetic ammonia manufacture. H. S. TAYLOR. *Chem. Met. Eng.* 27, 1263-6(1922).—The liquefaction, the water-gas catalytic, the steam-iron, and the electrolytic processes are discussed. The major cost of production is in the purification of the gases. For successful competition in NH_3 synthesis the power costs must be below 2.5 mils per kw.-hr.

W. H. BOYNTON

The production of ammonia from nitrogen and hydrogen. FRITZ HABER. *Naturwissenschaften* 10, 1041-9(1922).—The Nobel prize address.

C. C. DAVIS

Annual report of the acting director of the Fixed Nitrogen Research Laboratory for the fiscal year ended June 30, 1922. F. G. COTTRELL. U. S. Dept. Agr., *Fixed Nitrogen Research Lab.* 1922, Sept. 10 pp.—Most of the work of the lab. has been done on NH_3 -synthesis catalysts, on which extensive and valuable data have been collected. A critical study of the cyanamide process has been made, as well as a general survey of the cyanide process. A little work has been done on the arc process.

F. C. Z.

The nitrogen industry in the United States. HARTLAND SEYMOUR. *Chem. Age* (London) 8, 6-8(1923).—A brief review of the Muscle Shoals plant, a repetition of the connection among explosives, dye and poison gas manuf., and a somewhat fuller study of the nitrate needs of the various crops in the U. S. Wheat, oats and corn annually remove 2,250,000 tons N from the soil, whereas only 11% of this is met by coke ovens, tankage and Chile nitrate.

F. C. Z.

Waste still liquor in ammonia-soda works. MOTOTARO MATSUI. *J. Chem. Ind.* (Japan) 24, 1386-94(1921).—To study the efficiency of different NH_3 -soda works, M. analyzed several samples of waste-liquors collected from the different parts of the works. Samples taken were 4 (A, B, C, D) of Syracuse Solvay Co., Albany museum; 1 (E) of La Madelein, Duchemia; 1 (F) of Dieuze, Schreib Soda Fabrikation; 1 (G) Northwich; 1 (H) of Middlewich, and 1 (I) of Makiyama. The results are resp.: d. 1.074, 1.056, 1.151, 1.071, 1.096, 1.105, 1.113, 1.111, 1.047; NaCl (g. per l.) 23.31, 22.90, 36.04, 22.42, 60.50, 70.50, 48.90, 53.50, 28.70; CaCl_2 (g. per l.) 55.54, 54.00, 92.29, 61.24, 72.80, 70.90, 110.80, 97.20, 35.70; $\text{Ca}(\text{OH})_2$ 6.57, 7.02, 33.40, 12.12, 4.72, 6.55, 4.86, 3.30, 8.33 g. per l.; CaCO_3 17.00, 5.50, 13.96, 8.04, 9.15, 8.55, 6.95, 8.30, 7.55; CaSO_4 1.25, 1.80, 8.03, 1.05, 5.09, 2.07, 3.15, 3.51, 2.50; $\text{Mg}(\text{OH})_2$ 4.71, 3.53, 11.87, 4.77, 3.35, 5.21, 3.38, 2.56, 3.48; SiO_2 , etc. 3.77, 0.19, 3.41, 3.20, 0.33, 0.51, 0.39, 0.58, 0.076; NH_3 0.0094, 0.0085, 0.0064, 0.007, 0.0119, 0.0176, 0.0119, 0.0102, 0.0201; the degree of con-

version of NaCl, 71.5, 71.3, 72.7, 74.0, 56.7, 51.1, 70.1, 65.5, 56.3; the waste liquor calcd. from conversion degree of NaCl for 1000 kg. of soda ash 19.05, 19.55, 11.47, 17.28, 14.70, 14.75, 9.6, 10.78, 29.9 cu. m.; loss of NH_3 in the waste liquor 1000 kg. of soda ash 716 (as SO_4) 665, 294, 563, 708, 302, 417, 440, 2404 g. The consumption of CaCO_3 and NaCl used in the still per unit quality of soda ash, and the rate of sedimentation of the waste liquors are also given.

S. T.

Magnesium chloride manufacture and the Pioneer Magnesite Works. B. S. LAL-KAKA. *J. Indian Ind. Labour* 2, 435-43(1922).—A description of the development of the Indian MgCl_2 industry started at Kharaghoda in 1914. MgCl_2 is prepd. from bitterns left in the pans after the manuf. of NaCl from brines from the Runn of Cutch. The av. compn. (5 analyses) of these brines is: NaCl 14.67, MgCl_2 4.63, MgSO_4 0.48, CaSO_4 0.44, KCl 0.41, CaCO_3 0.01, MgBr_2 0.07%.

A. PAPINEAU-COUTURE

The deterioration of sublimed sulfur as a result of aging. FONZES-DIAON. *Prog. agr. vit.* 78, 378-81; *Ann. fals.* 15, 459-62(1922); cf. C. A. 11, 690.—Samples of several grades of sublimed S, preserved over a period of 9 yrs. showed only a small decrease in the % insol. in CS_2 , ranging from 5.2% for a very pure product, with original content of 32.7%, to 1.4% for a crude prepn. with original content of 10%. A low CS_2 -insol. content in such products cannot be attributed to aging in storage.

P. R. DAWSON

Helium in the U. S. A. R. B. MOORE. *Nature* 111, 88-91(1923).—Natural gas from the Petrolia, Texas, field runs as high as 1.5% He, but most gases are less rich than this, some contg. only 0.1-0.2% He. The He belt extends from Texas through Oklahoma, south-eastern Kansas, southern Illinois, and from there through Ohio into Penna. and N. Y. There is also He-bearing gas in Indiana, Kentucky and West Virginia. The richest gas is in Texas, Oklahoma and Kansas. Two plants were established at Fort Worth in 1918, using the Linde and Claude systems, resp. The Linde plant is now producing about 15,000 cu. ft. 93 to 95% He per day. A third plant, using the Jefferies-Norton process, erected at Petrolia in 1918, was shut down in 1921. Two plants have been built to repurify He that has been used in balloons and dirigibles. In one of these plants, built on two railroad cars, charcoal purifiers are used in conjunction with refrigeration, resulting in the production of He practically 100% pure.

E. G. R. ARDAGH

Carbon tetrachloride as a fire extinguisher. JACQUES FOHLEN. *Technique moderne* 14, 593-6(1922).— COCl_2 is formed only at 200-800°; dry air can react with CCl_4 according to the equation $\text{CCl}_4 + \text{O} = \text{COCl}_2 + 2\text{Cl}$, but the yield is very small (max. obtained 0.55%, theoretical 64%); in the presence of combustible org. matter the reaction $\text{C} + \text{O} + 2\text{Cl} = \text{COCl}_2$ takes place, but the yield is again very small (max. obtained 0.75%, theoretical 128%); moist air reacts thus: $\text{CCl}_4 + \text{H}_2\text{O} = \text{COCl}_2 + 2\text{HCl}$. The yield at 300° is nearly quant. (64%). Hence, CCl_4 fire extinguishers should be used only in fairly well ventilated places, and should not be used in a moist atm., and water should never be used immediately after CCl_4 to cool down objects.

A. PAPINEAU-COUTURE

TAYLOR, R. L.: **Bleaching Powder and its Action in Bleaching.** Manchester: John Heywood, Ltd., 121 Deansgate, Manchester. 78 pp. 4s. 6d. Reviewed in *Chem. Trade J.* 71, 770(1922).

Technical Records of Explosives Supply, 1915-18. VII. Manufacture of Nitric Acid from Nitre and Sulphuric Acid. London: H. M. Stationery Office. 86 pp. 11s. Reviewed in *J. Soc. Chem. Ind.* 41, 429R(1922).

Explosions in liquid-air rectification plant (FYLEMAN) 24. Analytical methods in phenol-aldehyde condensate manufacture (ORMANDY, CRAVEN) 7. Manufacture of

H₃PO₄ in the electric furnace (SWANN) 4. Manufacture of baryta for treating molasses (DEGUIDE, BAUD) 28. Producer furnace for heating aluminium chloride stills (U. S. pat. 1,440,857) 21.

Sulfuric acid. T. SCHMIDEL and H. KLENCKE. Brit. 187,016, July 12, 1921. Addn. to 149,648 (C. A. 15, 414). The process described in the principal patent is modified as follows to obtain an acid of higher concn. In one modification a soln. of nitrosylsulfuric acid of above 58° Bé. is supplied to each unit of the plant, a more elevated temp. being employed if necessary. In a second method, the central part of the plant is irrigated with a soln. of nitrosylsulfuric acid of a lower concn. than that used in the fore and rear parts of the plant. The second method may be further modified by adding H₂O to the units in the middle of the plant, the N oxides consequently liberated being recovered by subsequently irrigating with acid of the same concn. as that employed in the fore part of the plant. Cf. C. A. 17, 185.

Hydrochloric acid and magnesia from magnesium chloride. CHEMISCHE FABRIK BUCKAU. Ger. 341,967, Oct. 11, 1921. MgCl₂ in the form of waste lye from the potash industry is mixed with MgCO₃ (preferably pptd.), and at high temperature is exposed to the action of steam. The HCl is driven off quickly and at a lower temp. than in the ordinary process and the MgO is left in the form of powder. A mixt. of MgCO₃, MgCl₂ and CaCO₃ or a mixt. of MgCl₂, CaCO₃ and MgSO₄ may be used. MgO and CO₂ alone or together with a mixt. of CaO, MgSO₄, and CO₂ also may be used.

Liquefaction of chlorine mixed with other gases. FARBWERKE VORM. MEISTER LUCIUS & BRÜNING. Ger. 305,652, June 16, 1921. The condensation of the Cl is so conducted that by gravity the condensed Cl comes into zones in which the partial pressure of the gaseous Cl in the gas mixt. is always a little higher than the vaporization pressure of the liquified Cl.

Purifying hydrofluoric acid. H. HOWARD. U. S. 1,439,960, Dec. 26. See Brit. 186,606 (C. A. 17, 327).

Apparatus for concentrating chamber acid. L. D. LANSDALE. U. S. 1,442,672, Jan. 16. Chamber acid to be concd. is passed through a symmetrically heated unit formed of pipe-like sections (arranged step-wise and electrically heated) and the fumes evolved are led to a collecting chamber and condenser.

Caustic alkalies. C. DEGUIDE. U. S. 1,440,211, Dec. 26. A Ba polybasic silicate, *e. g.*, bi- or tri-barytic silicate is decomposed by H₂O and Na₂SO₄ or K₂SO₄ at a temp. of about 80° in order to form NaOH or KOH. The polybasic silicate is regenerated by heating the solid reaction residue with C at 1400°. Cf. C. A. 16, 2391.

Alkali metal cyanides. F. J. METZGER. U. S. 1,439,909, Dec. 26. A crude furnace product obtained by heating a mixt. of alkali metal carbonate, C and Fe with N is treated with CO₂ to effect release of HCN without polymerization and the HCN caused to react with alkali metal carbonate at a temp. of 200-500° to form cyanide.

Chrome alum. CHEMISCHE FABRIK IN BILLWARDER VORM. HELL & STHAMER AKT.-GES. AND P. HASENCLEVER. Brit. 187,231, Oct. 12, 1922. Chrome alum crystals are prepd. by adding to green chrome alum soln. small quantities of K₂Cr₂O₇, H₂SO₄ and H₂SO₃, when the violet chrome alum is immediately produced and is readily crystd. The quantity of K₂Cr₂O₇ is not sufficient to oxidize any Fe present and the H₂SO₃ is equiv. to the K of the dichromate. *E. g.*, Fe-Cr is dissolved in H₂SO₄, and about half of the FeSO₄ is removed by crystn. The FeSO₄ is sepd. in a centrifugal machine and the necessary quantity of K₂SO₄ is then added. The green soln. is then treated as above described to obtain chrome alum crystals.

Chrome alum. CHEMISCHE FABRIK IN BILLWARDER VORM. HELL & STHAMER AKT.-GES. AND P. HASENCLEVER. Brit. 187,232, Oct. 12, 1922. Fe-Cr is dissolved

in H_2SO_4 or HCl , and an alkali hydroxide or carbonate is added in quantity sufficient to ppt. the Cr as hydroxide free from Fe. The ppt. is washed and dissolved in H_2SO_4 , and K_2SO_4 is then added to produce chrome alum.

Lead chloride, sulfate, and peroxide. A. NATHANSOHN. Brit. 187,195, Nov. 28, 1921. Ores, etc., contg. Pb, preferably contg. or with addn. of oxidizable S, are treated in the presence of dissolved chlorides with Cl or hypochlorites at a low temp. until the Pb is converted into tetrachloride and dissolved. Ag chloride remains with the residue and may be extd. with thiosulfate. The soln. is sepd. and the surplus Cl is blown out or reduced by reducing agents to obtain PbCl_2 or PbSO_4 , or the soln. is neutralized or rendered alk. to obtain the Pb as peroxide. After the sepn. of the Pb the Cu may be removed by cementation or electrolytically and the Zn electrolytically or by pptn. as hydroxide with CaO . Carbonate ores may also be leached with the acid liquor to neutralize the liquor and ext. ingredients from the ores. The reducing agents mentioned are wastes contg. Zn or Fe, oxidizable salts such as ferrous salts, H_2SO_3 or its salts, H_2S , sulfides, thiosulfates, or org. reducing agents such as sulfite cellulose waste liquor. When H_2SO_3 is used the Pb is pptd. as sulfate.

Utilizing the waste magnesium chloride lye from the potassium industry. CHEMISCHE FABRIK BUCKAU. Ger. 302,350, Dec. 12, 1917. By the processes of Ger. 283,096, 284,177 and 290,876 (C. A. 17, 187) not only can all the Cl be removed as HCl from MgCl_2 but also from the alkali chlorides, provided these are distd. in mixt. with MgSO_4 . In this process the MgSO_4 may be replaced by a mixt. of MgCl_2 and H_2SO_4 . The sulfates of the alkali and Mg are either sepd. in the usual manner or utilized as double salt. Naturally occurring double chlorides of alkali and Mg may be utilized in the manner indicated.

Titanium chloride, oxide, and sulfate. G. CARTERET and M. DEVAUX. Brit. 184,948, June 27, 1921. Ti ores contg. Fe are reduced and chlorinated in such a manner that the Ti chloride is obtained separately from the other products of the process. The ore is heated in a retort at 800° for 1 or 2 hrs. in the presence of a slow current of reducing gas or by means of C. Dry Cl is passed through the furnace heated to 350° . At this temp., the Fe only is attacked, and the FeCl_3 formed passes out and is collected. The direction of the Cl current is then reversed, and the temp. raised to 550 – 600° . The Ti is attacked, and the Ti chloride, contaminated with traces of Fe, Si, etc., passes out through another opening. The Ti chloride is purified by distn., and may be used for the prepn. of Ti sulfate and oxide. E. g., it may be dissolved gradually in dil. H_2SO_4 , yielding the sulfate, or the soln. so obtained may be dild. and boiled to yield the hydrated oxide. The HCl evolved in this last process is collected in an alk. soln., which is then electrolyzed to regenerate Cl and alk. soln. for re-use. The H_2SO_4 resulting from the hydrolysis of the sulfate may be used to treat a further quantity of chloride, thus rendering the process cyclic. The Ti chloride may be dissolved in cold water, and the soln. neutralized, e. g., with NaOH , to ppt. the oxide. The FeCl_3 may be heated to recover Cl for re-use, or it may be dissolved and reduced by means of iron sulfide, the S sepd. by filtration and the soln. electrolyzed to recover a further quantity of Cl.

Evaporating waste liquors containing calcium sulfate. C. T. WHITTIER. U. S. 1,422,317, Jan. 16. Liquor contg. CaSO_4 , e. g., the waste liquor obtained in manuf. of tartaric acid, is sprayed into a sufficient vol. of heated air to evap. the moisture and facilitate recovery of K_2SO_4 . Immediately prior to spraying the liquor is maintained at a temp. low enough to prevent pptn. of CaSO_4 , to avoid incrustations.

Dry granular acid calcium phosphate. C. T. WHITTIER. U. S. 1,422,318, Jan. 16. A soln. contg. acid Ca phosphate is sprayed into warm air to evap. moisture, the pressure used in spraying being regulated in accordance with the size of the particles of dry phosphate desired. Products thus prepd. are suitable for use in *baking powders*.

Storage of sodium chloride. SANGORÔ SAITÔ. Japan 40,142, Sept. 30, 1921. A homogeneous mixt. of dried and powdered Al silicates 27, kieselsguhr 63, potash 9, and CaO 1 is pressed to a suitable form. NaCl is kept dry by storage on a layer of the mixt.

Hydrogen peroxide. DEUTSCHE GOLD- & SILBER-SCHIEDRANSTALT VORM. ROESSLER and O. LIEBKNECHT. Brit. 186,871, Feb. 16, 1922. H_2O_2 of more than 10% strength is obtained in one operation by treating an alkali perborate with a mineral acid such as H_2SO_4 , HCl, or H_3PO_4 , with agitation. Boric acid and the salt produced, such as Na_2SO_4 , sep. The perborate may be added to the concd. acid, or the acid to a suspension of the perborate.

Hydrogen peroxide. WOODLANDS, LTD. Brit. 186,840, Oct. 12, 1921. H_2O_2 is distd. from solns. contg. or yielding it by bringing the solns. into contact with the highly heated surface of a liquid or a fused salt, the evolved vapors being rapidly condensed. The liquid or fused salt employed is such that it can be heated, without boiling, to a temp. higher than the b. p. of the soln. to be distd.; the soln. is then directed on to the heated surface either as a thin sheet or, preferably, as a spray; a stream of air may be sucked through the liquid to prevent sudden frothing. The preferred material for the heated surface is H_2SO_4 or a fused bisulfate. Crude solns. of H_2O_2 , Na, K, or NH, persulfate, persulfuric acid, and inorg. peroxides are given as examples of solns. which may be treated by the process.

Hydrogen sulfide. H. HOWARD. Brit. 187,592, Oct. 3, 1922. See. U. S. 1,435,471 (C. A. 17, 453).

Phosphorus. R. FRANCHOT and K. P. McELROY. U. S. 1,441,573, Jan. 9. Air is blown into a preheated charge which may be formed from phosphate rock, a silicate and C, the air being sufficiently heated to produce slagging temps. in the mixt. Free P is condensed from the resulting gases and vapors.

Nitrogen fixation. K. P. McELROY. U. S. 1,441,695, Jan. 9. A stream of molten Na_2CO_3 or K_2CO_3 is brought into contact, countercurrentwise, with hot producer gas in the presence of C and Fe to form cyanide.

Nitrogen fixation. K. P. McELROY. U. S. 1,441,693, Jan. 9. A contact mass formed from Co, Ni or Fe and baryta or other alkali is alternately exposed to action of hot gases contg. N and CO, e. g., producer gas, and to the action of steam. C is first deposited from the CO and cyanide is then formed with the N.

Bleaching mixture. ISUKE TOMINAGA. Japan 40,138, Sept. 30, 1921. A homogeneous mixt. of $CaOCl_2$ 2, $NaHCO_3$ 1, acid clay 1, and a small quantity of perfume and blue dyestuff.

Waterproofing composition. C. D. SHAFFER. U. S. 1,441,605, Jan. 9. A compn. adapted for waterproofing leather, textile fabrics or metals is formed of "cumar" 1, rubber 2, paraffin 2 and a light hydrocarbon oil such as gasoline 20 parts.

Coating composition. H. H. WARMUND. Brit. 187,611, Oct. 18, 1922. A compn. particularly adapted for sealing bottles consists of an agglutinant such as glue or silicate of soda, an earthy filling material such as talc, and an aq. soln. of soap and wax. A capsuling-mass consists of 10 parts of leather glue diluted to 28-35° Bé. mixed with 20 parts of talc and 3 parts of a soln. contg. 25 g. of hard soap and 40-50 g. of carnauba wax per l. Coloring matter may be added.

Mixture for sealing and coating. H. H. WARMUND. U. S. 1,442,752, Jan. 16. A mixt. adapted for sealing receptacles is formed of 3 parts of an aq. soln. contg. carnauba wax 4-5% and hard soap 2.5%, 10 parts of a liquid leather glue of 28-35° Bé. and 20 parts by wt. of talc.

Plastic composition. J. F. E. GRANET. Brit. 187,376, Aug. 13, 1921. A white compn. suitable for elec. insulation and other purposes consists of carnauba wax 40,

copal or sandarac 5, powd. mica 40, lithopone 15, to which may be added borax 3 parts.

Plastic product from blood. F. W. V. FITZGERALD. U. S. 1,441,570, Jan. 9. Fluidity of blood is preserved by addn. of a citrate and the preserved blood, without prior coagulation, is partially dehydrated at a temp. of about 49° or lower and then thoroughly exposed to air and coagulated by CH_2O or other reagent to form a solid material adapted for use in making molded articles. Cf. C. A. 17, 189.

Condensation products from formaldehyde and urea. H. GOLDSCHMIDT and O. NEUSS. Brit. 187,605, Oct. 17, 1922. Turbid materials, resembling meerschaum and porcelain, are produced by condensing urea with not more than 120% of HCHO in the presence of at least 3% of acid, the proportions being calcd. on the pure anhyd. material in each case. The products are easily worked, and being porous, may be impregnated with coloring solns., oils, resins, salt solns., etc. Examples are given in which urea is dissolved in HCHO soln., the soln. heated to effervescence, HNO_3 , H_2SO_4 or HCl then added, and the whole finally emptied into molds.

Laminated sheets comprising phenolic condensation products. J. M. TAYLOR. U. S. 1,441,133, Jan. 2. Two sheets of parchmented fiber contg. a phenolic condensation product in an intermediate stage are applied to the opposite sides of a sheet of parchmented fiber and the 3 layers of material are then subjected to the action of pressure and heat sufficient to consolidate them and convert the condensation product into final insol. form. Sheets thus formed are suitable for making gears or elec. insulators.

Absorbent carbon from phenolic condensation products. L. WALLERSTEIN. U. S. 1,442,372, Jan. 16. A material adapted for absorbing gases or decolorizing solns. is prepd. by carbonizing phenol-formaldehyde condensation products at a temp. of about $800\text{--}900^{\circ}$.

Shoe-cleaning composition. A. J. SCHULTZ. U. S. 1,439,915, Dec. 26. ZnO 1–1.5 lbs., benzine 1–1.5 teaspoonfuls, mucilage 5–8 drops, "toilet water" 1–2 oz. and soft H_2O to make a total of 1 gal.

Shoe polish. A. MACH. U. S. 1,432,707, Oct. 17. Cascin 20 oz. is added to a boiling soln. of H_3BO_3 0.75 oz. in soft H_2O 2 gals., the mixt. is evapd. to 1 gal. and is then mixed with 0.5–1 oz. of a coloring material such as "union brown" or "union wine."

Fire-extinguishing composition. A. HENNING. U. S. 1,440,918, Jan. 2. A fire-extinguishing mixt. is formed of MeBr mixed with CCl_4 , CHCl_3 or CH_2Cl_2 or similar liquid of higher b. p. than the MeBr .

Foam for preventing or extinguishing fire. G. H. L. KENT. U. S. 1,441,728, Jan. 9. A foam adapted for extinguishing fires is prepd. by mixing a soln. contg. $\text{Al}(\text{SO}_4)_3$, FeSO_4 or a similar salt with a soln. contg. NaHCO_3 and Na soaps of sludge sulfonic acids from mineral oils.

"Anti-freeze" cooling and refrigerating solution. N. A. DUBOIS. U. S. 1,442,330, Jan. 16. A soln. adapted for use in automobile radiators is formed of CaCl_2 , H_2O and a small amt. of Zn chromate to prevent corrosion.

Treating spent decolorizing carbon. A. WIJNBERG. U. S. 1,440,194, Dec. 26. Spent decolorizing C is heated in successive stages at increasing temps. and gases and suspended particles produced are subjected to condensation to remove moisture and recover the suspended revived C. U. S. 1,440,195 relates to an *app.* for carrying out this process.

Absorbent for gases. C. P. MCNEIL and E. P. BROWN. U. S. 1,441,696, Jan. 9. A hard, porous, non-deliquescent absorbent of high activity and capacity, adapted for use in gas masks is formed by reaction between $\text{Ca}(\text{OH})_2$, NaOH , kieselguhr, active C and H_2O .

Sound-reproducing devices. J. W. BARSTOW. Brit. 187,049, July 26, 1921. Prepd. skin for diaphragms, sound-plates, and amplifiers for gramophones consists

of raw animal skin soaked in H_2O until supple and then in a soln. of alum or formalin in H_2O , then stretched until dry, smoothed, and finished with French polish, or amyl acetate, gum copal, or ordinary varnish.

Purifying graphite. M. LANGHEINRICH. Brit. 187,080, Aug. 20, 1921. Natural graphite is purified from deleterious admixts. such as SiO_2 , Al_2O_3 , pyrites, mica, etc., by mixing intimately with pulverized coal, charcoal or coke, and heating electrically in a retort to $2,200^\circ$ or over. The proportion of coal required is calcd. on the amt. of impurities present so that the coal will be sufficient to unite with all the O and metallic ingredients. Al, Fe, Si and S are in turn volatilized and may be collected in the form of their oxides in sep. receptacles opened for the purpose. The SiO_2 is useful as a filtering substance, a polishing powder. etc., the SO_2 for the manuf. of H_2SO_4 and the metallic oxides for metallurgical purposes.

Metal and color foils. DIAMOND DECORATIVE LEAF CO. Brit. 186,889, March 20, 1922. Paper, etc., treated with an alkali metal silicate such as waterglass is used as a backing for beaten metal foils, as a backing on which bronzing and color films are produced by spraying, or as a substitute for gold-beaters' skin. For the latter purpose, to increase the pliability of the leaf, the silicate may be mixed with glycerol or castor oil. Foil or leaf carried by the treated paper will, upon heating under pressure of a die, become detached from the backing and, together with a film of silicate, become attached to the material it is desired to stamp.

Treating seaweed. P. T. FREUNDLER. Brit. 187,970, Oct. 24, 1922. Seaweed is heated at about 100° with a satd. soln. of Na bisulfite to obtain a liquor contg. I and sugars, gums, etc. The residue is treated with a dil. soln. of Na_2CO_3 to obtain a liquor contg. algin, and a residue of cellulose impregnated with agglutinants. The bisulfite liquor is mixed with CaO to ppt. Ca sulfite and the sepd. liquid is treated by the usual processes to obtain I and fermentable products. The alk. soln. is decolorized, alginic acid is pptd. by a mineral acid, filtered, washed and dissolved in NH_3 , the soln. being evapd. or transformed into Na alginate. The residue is washed and dried and becomes a mass analogous to paper pulp, which can be molded or compressed.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

C. E. BARTON, C. H. KERR

Study of glass. III. KIYOHITO HAGIWARA, KAN-ICHI MORIMOTO, KIYOSHI UEDA AND TAITARO HIRAOKA. *J. Japan. Ceram. Assoc.* **362**, 457-88(1922).—Nakazawa, *et al.* (*C. A.* **14**, 1419) attributed the dimming of mirrors to minute spots on the surface of glass. When a piece of window glass was heated to $350-600^\circ$ for 1-2 hrs. in an elec. furnace, it was covered with minute particles which increased in amt. with the time of heating. They grew rapidly at 650° and disappeared almost completely at temps. over 800° . Their amts. diminish in repeating the process, if they are wiped off every time, and also their growth ceases completely or nearly so after the minute particles have once been erased with a piece of wood or steel. Similar minute particles appear also at ordinary temp., though it requires a much longer time, usually more than 3 days. They must not be confused with the products of weathering. They grow uniformly scattered, in dendritic crystals or groups, the latter 2 aggregates being probably caused by the atm. moisture. The substances, exuded at ordinary or higher temps., are hygroscopic and form hydrated crystals, which sustain efflorescence as days pass. Microscopic examns. of these substances before and after treating with HCl or $CaCl_2$, indicate that they are mainly Na silicate, sometimes containing Na_2SO_4 . The amts. of the substances exuded from window glass when new specimens were heated at $480-520^\circ$

in a muffle kiln for 1, 5 and 10 days, were 0.0035%, 0.0052% and 0.0088% of glass, resp. In the cylinder process of mfg. window glass the drawn cylinders are sometimes covered with minute particles, though it happens only rarely. Some cylinders which broke in drawing have shown striped growth of the particles which is more common with window glass made by Fourcault's or Colburn's process. Such a glass is very brittle and breaks usually in thelehr. The authors believe that the minute particles are exuded from glass owing to its unstable state of equil. Some pores in glass have much exudation while others show it only after heating at a temp. over 400°. Glass for good mirrors must be polished to remove the exudation baked on its surface or has to be examd. with a vitroscope before it is silvered. S. KONDO

High-grade clays of the eastern United States with notes on some western clays. H. RIES, W. S. BAYLEY, *et al.* U. S. Geol. Survey, *Bull.* 708, 305 pp. (1922).—Statistics of production, imports and exports are given. Over 80 chem. analyses of the various clays are recorded, principally those from deposits in Pa., Va., Fla., Ala., Miss., Tenn., Ky., Ill., and Ark. Mineralogical comps., phys. tests and fire tests are tabulated in large numbers. The requisite qualities of high-grade clays for different purposes are specified. The deposits of kaolins or white residual clays are discussed in 114 pages, residual clays of undetd. derivation in 32, Indianaite in 15, sedimentary clays of the Coastal Plain and the Embayment area in 129 and the microscopic study of clays in 13.

L. W. RIGGS

Clays. I. Fundamental materials and their chemical composition. O. BOUDOUARD AND J. LEFRANC. *Bull. soc. chim.* 31, 976–82 (1922).—One anhyd. compd., $Al_2O_3 \cdot SiO_2$, is known to exist under 3 different cryst. forms, namely, andalusite, cyanite and sillimanite. Hydrated silicates are: $Al_2O_3 \cdot SiO_2 \cdot 6H_2O$, allophane, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, kaolinite, and $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$, pyrophyllite. The purpose of this study is to det. the factors by which the ceramic qualities of clays may be judged and to throw light upon their origin and history. Samples A and B from England, C and D from Germany and E, F, G, H, I from France are described as to their phys. properties. Chem. analysis gave the following results:

	A.	B.	C.	D.	E.	F.	G.	H.	I.
SiO ₂	46.20	47.27	46.00	61.15	47.51	71.02	50.50	44.87	50.30
Al ₂ O ₃	38.89	38.71	39.80	28.92	35.78	19.78	31.77	37.93	31.63
Fe ₂ O ₃	0.81	0.33	tr	0.88	0.60	0.98	0.43	0.85	1.29
CaO	tr	0.14	tr	tr	0.41	0.41	tr	0.47	3.49
K ₂ O	1.47	0.25	0.70	2.45	4.47	0.40	0.26	0.14	2.09
Na ₂ O	0.46	1.12	tr	0.37	0.16	0.30	0.03	0.13	1.02
H ₂ O	12.63	12.40	13.75	7.03	11.23	6.85	12.54	15.44	9.48

L. W. RIGGS

Dutch gold (imitation gold leaf). P. P. BUDNIKOFF. *Z. angew. Chem.* 35, 653 (1922).—The prepn. used chiefly for applying gilt to glazed ceramic products is made by boiling turpentine with 20% S on an oil bath, with reflux condenser, and adding AuCl₃ to the product. After some hrs. a red-brown liquid is formed which contains 0.4–14.6% S, depending upon the fraction collected, while about 50% of the turpentine remains as a resin. Const.-boiling substances have not been isolated from the distillate, but by acting upon it with CH₃I, and purifying by dissolving in EtOH and pptg. with Et₂O there is obtained C₁₀H₁₆SCH₂I, *methylmercaptoisulfonium iodide*. With moist Ag₂O this yields a base which ppts. heavy metals and expels NH₃ from NH₄ salts. It decomposes on boiling with H₂O, giving an oil, probably C₁₀H₁₆S, which easily takes up S to form polysulfides. Upon adding alc. solns. of salts of heavy metals there are formed difficultly sol. ppts., amorphous, and unstable, which give metallic sulfides upon heating or boiling with H₂O. Such a ppt. from AuCl₃ does not give a suitable gilt, as the grains are probably

too large to form a coherent film. If an aq. soln. of AuCl_3 is treated with the terpene sulfide, the former gradually dissolves, forming a colloidal Au soln. This prepn. gives a black mirror of Au_2S_3 when heated to $250\text{--}300^\circ$ in a muffle, and a beautiful güt at a higher temp. Still better results were obtained from the action of S_2Cl_2 on turpentine, effective cooling being necessary. The theoretical explanation of this reaction is not clear.

W. C. BRAUGH

The absorption test on common brick. SHIJI KONDO AND MASARU NAKAO. *J. Japan. Ceram. Assoc.* **363**, 527-51 (1922).—Samples were supplied by the Nippon Brick Mfg. Co., Tokyo, and the Osaka Ceramic Industries Co., Osaka. They classify their common bricks into 8 and 6 grades, resp., according to the degree of burning. The porosities of the Tokyo bricks were 27.04-38.87%, while those of the Osaka bricks were 23.27-32.61%. The rate of drying of bricks previously soaked in H_2O for 48 hrs. or longer was studied to find the best method for drying. The time required for drying decreases as the temp. rises, e. g., the mean values for the Tokyo bricks were 7.25, 6.94, 6.63, 5.13 and 4.13 hrs. at 100° , 110° , 120° , 130° and 140° , resp. The rate of drying diminishes rapidly as the % H_2O decreases and the time required for drying does not follow the order of absorption. If bricks are considered dry when the wt. of brick has become const. for 2 hrs., as is very usual, the dry wt. is affected by the temp. in the drying oven, unless a very sensitive balance is used. Thus, the 8 grades of the Tokyo bricks had 0.08, 0.06, 0.01, 0.01 and 0.00% H_2O (av.) after drying at 100° , 110° , 120° , 130° and 140° , resp., and 6 grades of the Osaka bricks showed 0.17, 0.07, 0.01 and 0.00% H_2O (av.) after drying at 115° , 120° , 125° and 130° , resp. These results indicate that bricks should be dried at a temp. not less than 125° . If dried bricks are weighed hot, the observed wts. must be a little less than those obtained by weighing them after they have been cooled in desiccators. The difference amounted to 0.39 g. or 0.02% for the Tokyo bricks (av. of 80 weighings) and 0.55 g. or 0.02% for the Osaka bricks (av. of 36 weighings). Therefore, hot bricks may be weighed in the absorption test. To see the rate of absorption, the dried Tokyo bricks were laid flat in a vessel and then H_2O was poured in it to a certain level. After 24 hrs., the level was raised to a certain height and kept for 24 hrs. more. During these 48 hrs., the progress of absorption was studied by weighing the bricks 15-18 times. The results are: (1) The depth of H_2O evidently affects the absorption, e. g.

Depth of H_2O in cm.....	1.0	2.9	5.5	8.8
Mean absorption in 24 hrs.....	14.26	14.19	14.15	14.01%
Cm. depth of H_2O during first 24 hrs... 1.0	1.0	2.9	5.5	8.8
Ditto during next 24 hrs..... 8.8	35.8	8.8	8.8	8.8
Mean absorption in 48 hrs..... 14.58	14.49	14.41	14.42	14.29%

The mean thickness of the bricks was 5.8 cm. (2) The progress of absorption is not materially affected by the degree of burning. (3) The absorptions in the first hr. were 91.1-97.3% of those in 48 hrs. Various methods of soaking were compared. The best method is to dip 1 cm. of bricks, placed flat, for 24 hrs. and then to immerse them entirely, their upper surfaces being 3 cm. below the H_2O level. Absorption is influenced by taking out the brick for weighing during the testing time. The absorption of brick which had been soaked in H_2O for 48 or 72 hrs. increased 3.76-5.00% in the Tokyo bricks and 3.10-4.29% in the Osaka bricks when they were boiled for 5 hrs. Tests in which bricks were laid flat, on side or on end in H_2O have shown that the best way is to lay bricks flat. *Proposed method for absorption test.*—The test bricks shall first be weighed and then dried in an air bath at a temp. of 125° to 135° for 2 hrs. After removing from the drier they shall be reweighed at once. If the second wt. closely checks the first they shall be considered dry, but if it does not check the latter they shall be dried for 2 hrs. more. If the third wt. checks the second they are considered dry. In the case

of doubt the bricks should be subjected to further 2-hr. drying treatments until check wts. are obtained. The bricks shall be cooled to room temp. and laid flat in a vessel. They shall then be submerged in H_2O 1 cm. deep, and the H_2O level shall be kept const. for 24 hrs. Then more H_2O shall be added to the vessel so as to immerse the bricks entirely in it, their upper surfaces being 3 cm. below the H_2O level. Maintain this for 24 hrs. more. Then the bricks shall be reweighed after surplus H_2O has quickly been wiped from their surfaces with a wet cloth which has been wrung hard. All weighings shall be read to the nearest g.

S. KONDO

Electrically heated ceramic ware. A. STEINHARDT. Brit. 188,050, July 28, 1921. In the construction of an electrically heated ceramic vessel, the vessel after being fired is fitted with a heating resistance provided with terminals, the heating body being then covered with ceramic material having the same coeff. of expansion as the resistance and composed of the same materials as the vessel but with the addn. of fluxing materials which lower its sintering temp. below that of the heating resistance, after which the entire app. is again fired. The vessel is essentially made from kaolin, feldspar and quartz and the fluxes added to form the material may consist of the oxides of Mg, Na, Pb and B together with a little Na chloride and waterglass. For a vessel composed of clay 48, quartz 40, feldspar 12%, and provided with a heating body of nichrome the material may have the following compn. by wt. Na_2O 0.1, K_2O 0.3, MgO 0.4, CaO 0.2, Al_2O_3 0.4, SiO_2 2.6 parts, and 4 parts of the material used in making the vessel. Such a compn. may be obtained by using borax 120, MgO 50, chalk 40, sand 70, Na_2CO_3 20, feldspar 100, PbO 40, zettlitz kaolin 100, fluorspar 60, Na_2SiO_3 50 parts, and 150 parts of glaze appropriate to the porcelain mixt. The terminals are in a holder and are preferably arranged side by side at 90° to the handle. In a modification the vessel has a raised bottom with a spiral groove on the underside in which the heating wire is situated.

Treatment of clay. W. FELDENHEIMER and W. W. PLOWMAN. Brit. 186,855 Nov. 21, 1921. Addn. to 184,271 (*C. A.* 17, 194). The process described in the principal pat. is modified by using as a deflocculating agent a dil. aq. soln. contg. the pyrophosphate of an alkali base, *e. g.*, Na pyrophosphate. The clay may be subsequently recovered from its suspension by the process of flocculation described in 121,191 (*C. A.* 13, 647) or otherwise.

Clay flux for brick compositions. B. SCHMIDT. U. S. 1,442,585, Jan. 16. A flux for use with clay in brick manuf. is formed from pulverized glass, salt, pulverized granite and oxidized Zn.

Clay pavement. H. L. HADLEY. U. S. 1,441,342, Jan. 9. The surface of a formed clay pavement is fired to harden it.

Crystalline abrasive and insulating composition. H. A. RICHMOND and R. MACDONALD, JR. U. S. 1,442,773, Jan. 16. A homogeneous cryst. product contg. oxides of B, Al, Si, Fe and Ti is prepd. by fusing bauxite 100, H_3BO_3 5, ilmenite 2 and steel chips 10 parts and reducing the excess silica and Fe oxide present in the mixt. by heating with coke in an elec. furnace.

Crucible of chemical porcelain. H. D. LILLIBRIDGE. U. S. 1,441,690, Jan. 9. The pat. relates to the curvature of the wall of the crucible, which flares outwardly at its top.

Refractory materials. E. D. FROHMAN. Brit. 186,968, June 10, 1921. A refractory compn. consists of finely divided fireclay, a siliceous refractory substance such as ganister or asbestos, and a vegetable substance which acquires binding properties when moistened with H_2O , such as sulfite pitch (a by-product from the manuf. of sulfite pulp), dextrin, or gum arabic. The compn. is mixed with H_2O when required for use.

Refractory materials. Z. OLSSON. U. S. 1,442,413, Jan. 16. A refractory material adapted for crucibles or furnace linings is prepd. from bauxite 95 and bentonite 5%.

Refractory articles containing zircon. H. H. BUCKMAN and G. A. PRITCHARD. U. S. 1,440,766, Jan. 2. Muffles, crucibles or similar refractory articles are formed of zircon and carborundum.

Refractory articles containing zircon. H. H. BUCKMAN and G. A. PRITCHARD. U. S. 1,440,657, Jan. 2. Retorts, muffles or other refractory articles are formed of zircon and SiO_2 or clay.

20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILEY

Vertical automatic cement kilns. E. CANDLOT. *Chimie et industrie* 8, 1206-10 (1922).—A discussion of the merits and demerits of various types of vertical kilns, showing how the former are retained and the latter overcome in the Perpignani-Candlot kiln with rotary, planetary grate. The merits of this kiln are extolled, and more particularly its advantages over the rotary kilns. A. P.-C.

A spontaneous sulfatation of calcareous stones in urban centers. ANDRÉ KLING AND D. FLORENTIN. *Compt. rend.* 175, 962-4 (1922).—Many analyses of sound and crumbly portions of limestone monuments in the Paris neighborhood show that the disintegrated portion of the stone contains an excessive amt. of SO_3 . The dark crust or scum which forms in the crevices and on the relief portions of monuments consists chiefly of org. matter, SiO_2 and CaSO_4 , with very little CaCO_3 . The formation of the CaSO_4 is attributed to SO_2 in the Paris atm. brought down by rain and snow.

M. O. LAMAR

Waterproof cement shingles. ANON. *Chem.-Ztg.* 46, 1037 (1922).—A brief description, with 6 cuts, of a method of manuf. J. H. MOORE

The preservative treatment of timbers for industrial uses. E. S. PARK. *Raw Material* 6, 17-22 (1923).—Moisture is necessary for the growth of fungi; causes of the presence of excessive moisture in timber are listed. A preservative must be toxic to the fungi, and must penetrate the wood. The methods of application are reviewed. Means of seasoning wood, controlling the preservative, and the advantages of creosote or ZnCl_2 soln. are discussed. W. H. BOYNTON

DAVIS, ARTHUR C.: **Manufacture of Portland Cement.** 3rd Ed. revised and enlarged. Dublin: J. Falconer. 429 pp. 25s.

WATSON, J.: **Cements and Artificial Stone.** Edited by R. H. RASTALL. Cambridge: W. Heffer & Sons, Ltd. 131 pp. 6s.

Gas coke for sugar factories (lime kilns) (DECLUY) 28.

Cements. G. SCHLOESSER. Brit. 187,362, Aug. 8, 1921. The heat generated by the combustion of town refuse is utilized to burn CaCO_3 which is added to the residue of the refuse to form a cement or mortar. The CaCO_3 may either be added to the refuse before or during combustion, the resulting slag being granulated by H_2O or steam and ground up, or it may be calcined in a sep. chamber heated by the burning refuse, with the ash of which the CaO is afterwards mixed.

Cement. BÜHLER GEB. Brit. 187,579, July 21, 1922. Part of the slurry is burned in rotary kilns, the waste gases from which are used to dry another portion of slurry, enabling it to be burned in shaft kilns.

Concretes. A. KLEINOGEL. Brit. 187,582, Aug. 3, 1922. In concretes con-

sisting of cement and finely divided hard substances such as Fe, steel, or other metals, or carborundum, the ratio of hard substance to cement is given by the formula $(100 \pm 177.8x) / (54 \mp 76.2x)$, where x is the difference in in. between the diam. of the grains of hard substance and 0.03937 in., the upper signs referring to grains of larger size than 0.03937 in. and the lower signs to smaller sizes. Acid-proof cement may be used.

Dutch tiles with a lustrous surface. G. MADDALENA. U. S. 1,440,882, Jan. 2. See Brit. 174,603 (C. A. 16, 1846).

Hydraulic anhydrite residue. R. HENNICKER. U. S. 1,442,406, Jan. 16. A compn. which sets with hydraulic properties is prepd. by hydrating anhydrite in the presence of HCl, H₂SO₄ or other catalyst and washing and heating the product.

Mortar and artificial stone from town refuse. G. SCHLOESSER. Brit. 187,066, Aug. 8, 1921. Five incombustible portions of refuse are smelted with a suitable flux by heat from combustible portions and cast into blocks as *artificial stone*. Coagulated slag resulting from the combustion of the coarser matter is converted into *mortar* by granulating, mixing with CaO, contact salts, etc., grinding, and subjecting to a high temp. so as to disintegrate silicates. The slag which has not coagulated may be mixed with the mortar or in admixt. with lime may be pressed to form building stones.

Bricks. C. L. NORTH. U. S. 1,440,234, Dec. 26. Bricks are molded from a mixt. of ground clinker and ash from a coal furnace, lime and H₂O, and are cured with steam under pressure.

Building block composition. C. A. FOX. U. S. 1,442,764, Jan. 16. A heated mixt. of earthy and oleaginous materials such as earth and asphalt is extruded from a die press and cut into building blocks.

Floor covering material. W. E. SUMNER. U. S. 1,442,012, Jan. 9. A floor covering material is formed of a waterproofed flexible substance, e. g., felt impregnated with asphalt, with an underlying layer of a mixt. of montan wax, rosin, paraffin and pigment.

Plaster wall board. J. W. EMERSON. U. S. 1,439,954, Dec. 26. A plaster board is formed largely of plaster of Paris reinforced near its surface with wire cloth or similar material and waterproofed by a gypsum and stearate mixt.

Preserving wood. F. DOUGLAS and H. PHIBBS. Brit. 187,527, Jan. 11, 1922. The compn. consists of paraffin oil, turpentine, water, carbolic soap, creosol, and linseed oil. A small quantity of pepper and camphor may be added.

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

The connection of the research committee with fuel research. H. M. CRANE. *J. Soc. Automotive Eng.* 12, 207-9(1923).—A summary of the work accomplished in 1922 by the S. A. E. committee on motor fuel research. Data show that crankcase diln. may be a ready means of measuring the probable general effect of too heavy fuel but it cannot be assumed that it upsets lubrication in such a way as to make the use of a fuel causing a certain % of diln. out of the question or even economically impossible.

D. F. BROWN

Constitution of coal. R. LESSING. *Gas World* 77, 28-9(1922).—A brief review.

J. L. WILEY

Dopplerite. Composition of coal. V. TIDESWELL and R. V. WHEELER. *J. Chem. Soc.* 121, 2345-62(1922).—Dopplerite (D) belongs to the group of substances resulting from the natural decay of vegetable matter. It can be prepd. artificially from org. materials to which the terms ulmin and ulmic substances have been applied. A sample of D from Antrim Co., Ireland, consisting of characteristic dull and bright portions analyzed (dry basis): (a) "bright jelly"—ash 5.05, C 57.91, H 5.31, O 34.68,

N 2.10, S 0.70% and (b) "dull jelly"—ash 5.2, C 57.91, H 5.31, O 34.53, N 2.10, S 0.70%. Loss on drying as received at 105° in N 74.%; the ash contained SiO₂ 1.91, Fe₂O₃ 17.32, Al₂O₃ 2.89, MnO₂ 0.62, CaO 56.96, MgO 4.27, Na₂(K₂)O 4.6, SO₂ 10.63%, P₂O₅ and Cl traces. 90.1% of D after drying at 110° was sol. in 5% KOH. Successive treatment of dried D with CHCl₃, EtOH, Et₂O and Me₂CO extd., resp., 0.46, 0.96, 0.12, and 0.50%; pyridine extd. 3.5%. Slow destructive distn. between 150° and 600° *in vacuo* gave much H₂, CO₂ and CO with some gaseous paraffins; the liquid products based on ash-free and moisture-free D analyzed H₂O 28.0, NH₃ 0.05, bases 0.02, phenols 0.65, acids 0.14, neutral oil 0.327%. The distillate was acid with AcOH for distn. temps. up to 270°; above 270 it was alk. 75% of the phenols were creosols and 0.03 to 0.05% furfural was found. The large amts. of CO₂ and H₂O evolved indicate carboxyl or anhydride, and hydroxyl groupings, resp.; AcOH indicates acetyl groupings and MeOH methoxyl. The N is probably present as pyridine linked to large molecules; easily decomposed imino N was not found. D is probably formed as indicated by Maillard (*C. A.* 11, 2010); i. e., ulmins are produced by the condensation of sol. carbohydrates and amino acids resulting from bacterial decay of cellulose, starch and proteins. No reason was evident to prefer either the furan structure of the artificial ulmins advocated by Marcussen (*C. A.* 15, 2632), who has also shown a relation of this structure to the aromatic structure suggested by Eller and Kock (*C. A.* 15, 83), against the phenolic structure of natural ulmins proposed by Fischer and Schrader (*C. A.* 15, 1610) with the exclusion of either.

E. T. ERICKSON

The dopplerite of Raubling. H. WINTER. *Glückauf* 58, 1533-9 (1922).—The dopplerite occurs in black pea-sized pieces interspersed with yellow gummy granules, of d. 1.39-1.466. It absorbs with swelling 60% H₂O, which cannot be removed by pressure. Small amts. of humic acid and its salts can be extd. with H₂O. Conc'd. KOH dissolves it with a small residue. Heated with dil. HNO₃ a red-yellow ext. is obtained from this dopplerite. With petr. ether, C₆H₆ and toluene successively, a 0.34% yellow-green or brown extract is obtained. It contains 52.7% volatile, 32.0% coke, 12.7% H₂O and 2.7% ash. The ash is grayish yellow, gives in H₂O an alk. reaction and warmed in H₂O turns brown-red, through formation of Fe(OH)₃. Distn. gives 3.9% crude tar, 43.3% half-coke and 22.8% gas. Detailed data are given for analyses of the extns., ash constituents, distillates, etc.

C. C. DAVIS

By washing only a part of coal mined, lowest ash and sulfur and largest yield are attained. G. R. DELAMATER. *Coal Age* 22, 751-7 (1922).—A plant designed to handle coal from Pennsylvania mines operating in the same bed was redesigned to handle coals of varying quality from mines all over West Virginia and Pennsylvania. The original plant for washing all the coal consisted of 12 jigs, 3 settling tanks with Lubrig dewatering elevators and 3 Elmore centrifugal coal driers. With good coal, the washed product ranged from 86 to 89% with 8% moisture, 6.73% ash and 1.15% S. The new arrangement contains 4 W. S. Tyler Co. Hummer 6-ft. machines with 4-mesh electrically vibrated screens, 6 jigs, 1 settling tank with dewatering elevator and 1 Elmore drier. The final product constitutes 92.5-95% of the raw coal and has about 5% moisture, 6.73% ash and 1.15% S. Of coal crushed to pass openings of 1.05 inch square approx. 60% passes through 4-mesh screens with the washing of only approx. 40% instead of all the raw coal. A Hummer screen with total area of 30 sq. ft. will efficiently handle 80-110 tons of coal per hr. provided the moisture content does not exceed 10%. Charts show results of mixing washed coal above a certain size with unwashed coal below that size; S in each size of raw coal, washed coal and refuse; ash in each size of raw coal, washed coal and refuse; % reductions of S and ash with yield on each size; ash content when any 1 screen is used to select coal for washing from rest of coal; S content when any one screen is used to select coal for washing from rest of coal; raw coal retained on

screens; washed coal retained on screens, and refuse retained on screens. Data are given in tables on % of various sizes and ash and S content in each size for raw coal, for washed coal and for refuse. Data are given also for the determining of final coal mixtures.

ARTHUR L. DAVIS

Powdered coal: Its application and advantages. W. O. THOM. *Far Eastern Rev.* 18, 785-90(1922).—China has done little to conserve natural resources. Diagrams are given of furnaces and plant for the use of powd. coal.

WM. H. ADOLPH

Pulverized coal as a fuel. A. FOCH. *Rev. sci.* 60, 554-7(1922).—A review.

A. R. ALBOUZE

The calorific value of coal. G. W. H. MUS. *China J. Science & Arts* 1, 94-101 (1923).—Data from the analysis of 24 Chinese and Japanese coals are applied to det. the accuracy of the Gouthal formula for calcg. calorific value. Shanghai coals tend to give more B.t.u.'s than those indicated by the formula. Fifteen of the samples examd. contained 40% volatile matter. The peroxide calorimeter gave abnormally high values with coal contg. 25% ash. This was an error due to high ash content, and could be produced experimentally by adding ash in the bomb.

WM. H. ADOLPH

Graphical evaluation of the heating power of solid fuel. A. G. DRIESSEN. *Helv. Gas* 42, 279-86(1922).—Det. once for all the heating power of the "pure" fuel, i. e., without ash and moisture by the direct calorimetric method. The calorific value of a given sample is equal to $q(1-A-W)-600W$, where q is the caloric value of the "pure" fuel, A % ash and W % moisture. A and W must be detd. in each case by chem. analysis; q for 7 different Dutch coals is 8261 to 8563 cal. per kg. For other fuels the following calorific values are adopted: anthracite 8350 cal., gas coal 8000 cal., new peat 5000 cal., old peat 5700 cal., new brown coal 6200 cal., old brown coal 7400 cal., coke 8150 cal., wood 4500 cal. Various graphical systems show, without calcn., the calorific value of a given sample of fuel from A and W .

R. BRUTNER

The determination of the calorific value of liquid fuels. H. MOSS and W. J. STERN. *Engineering* 114, 729-31(1922).—Expts. were undertaken to investigate methods of detg. calorific values, with a view to evolving one by means of which abs. values for any fuel undergoing engine tests could be obtained quickly and accurately. Two methods are described with drawings of app. Both depend upon vaporization of the fuel, the vapor being burned and the resulting heat measured. In one method a Watson vaporizer and Boys calorimeter are utilized. The amt. of fuel consumed is measured by vol. and vaporization is accomplished by heat, corrections being made. The other method utilizes a stove with Primus burner and Junker's calorimeter. The stove is suspended from a balance and the fuel consumed is detd. by wt. Fuel is vaporized by air pressure and no correction is necessary.

H. C. PARISH

Calculation of the commercial calorific value of fuel. P. MAHLER. *Chimie et industrie* 8, 1175-6(1922).—Polemical against Fohlen (*C. A.* 16, 4045). **Reply.** Fohlen. *Ibid* 8, 1176-9. **Reply.** MAHLER. *Ibid* 8, 1179.—Discussion of definitions of calorific value and heat of combustion.

A. P.-C.

Discrepancies observed in determinations of the calorific power and the volatile matter of combustible solids. GOUTAL. *Rev. universelle mines* 14, 467-76(1922); *Rev. ind. minérale* No. 47, 337-8(1922).—An investigation of the cause of wide variations in the results on coal obtained by different labs. The ash and H_2O were close, but the calorific power detd. by a Mahler bomb varied 5% and the volatile matter 15%. The discrepancies in calorific power are laid to inaccurate temp. measurements, bad location of app., an incorrect H_2O equiv. and the presence of combustible gas in the O. Those in the detn. of volatile matter were due to lack of standard methods. It is recommended that (1) the sample be pulverized to pass a sieve of 225 meshes per cm.²; (2) 4-6 g. be used; (3) a porcelain crucible be used; (4) that it be protected from

the direct action of the flame by the use of an elec. furnace, double crucible or muffle; (5) the temp. be raised slowly to 1000° in 0.5 hr.; (6) this final temp. be kept const. for 0.25 hr.; (7) the temp. be allowed to drop to 200° before removing the crucible to a dry atmosphere. By this procedure variations are less than 0.001 of the wt. of the combustible.

C. C. DAVIS

Short method for the ultimate analysis of coal. S. W. PARR. *J. Ind. Eng. Chem.* **14**, 681(1922).—An ordinary combustion is made with Na_2O_2 in a calorimetric bomb or similar app. and the values of S and B.t.u. are found. The calcns. are then made by means of simple formulas as indicated with a degree of accuracy entirely commensurate with that secured by the longer process.

J. L. WILEY

Notes on the Hoffman potash test. J. H. H. NICOLLS. Can. Dept. Mines, *Summary Report No. 574*, 43-4(1922); cf. *C. A.* **12**, 1507, 2678.—An attempt was made to work out a modified test which would further differentiate between various lower grade coals. The following methods were tried: (1) diln. of the soln. obtained by boiling 0.5 g. of coal with the standard potash soln. (as in the general test) with definite vols. of water; (2) boiling 0.5 g. of coal with the standard soln. dild. with 1 or more vols. of water; (3) boiling 0.1 g. of coal with the standard potash; (4) boiling 0.1 g. of coal with the standard potash dild. with 1 or more vols. of water; (5) detg. what diln. of standard potash soln. was necessary in order to produce a certain definite color on boiling with a particular coal. Each of these methods indicated distinct differences between the low grade coals, but results by one method did not always place coals in the same order as did those from another. Contrary to expectation diln. of potash up to a certain limit increased its action on coal. Boiling 0.1 g. of coal with the standard potash proved the most satisfactory. The filter paper used should be tested with the potash to det. the amt. of color extd. With dil. solns. only the filtrate which passes through the paper during the first 15 min. of filtering should be considered. Ferric chloride referred to in the former paper means $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and its undild. soln. is No. 1 of the Hoffman series. **Trent process for purifying coal high in ash.** B. F. HAANEL. *Ibid* 45-54.—The process depends upon the selective affinity of oil for the carbonaceous matter and of water for the mineral ash content. The original paper should be consulted for a description of the machinery employed and the details of the procedure. The results of a treatment of 9 samples of Canadian lignite are tabulated.

L. W. RIGGS

The preparation and economic use of coals, particularly lignites. K. KEGEL. *Naturwissenschaften* **10**, 1014(1922); cf. *C. A.* **17**, 197.—Priority is acknowledged for Kempf in the use of certain graphic methods (*C. A.* **15**, 1795).

C. C. DAVIS

Dewatering of peat by pressure. J. W. HINCILEY. *J. Soc. Chem. Ind.* **41**, 365-8T (*Chem. Age* (London) **7**, 704-5; *Chem. Trade J.* **71**, 607-8(1922)).—The compn., properties and uses of peat are discussed. Raw peat contains 85-90% of water. This may be reduced to from 80 to 81% by cold pressing at a pressure of 50 lb. per sq. in. In drying peat by heat or air, the presence of the colloidal matter may be an advantage but in drying by pressure the colloidal property must be completely or largely destroyed. In suitable app. the water may be removed by pressure down to approx. 50% by only partly destroying this colloidal property. By warming by means of steam in a press to the b. p. of water and applying pressure rising slowly to 1000 lbs. per sq. in. the water content of a Norfolk peat was reduced below 50%. By cold pressing at 800 lb. and under the very best conditions a reduction in water content to only 75% was effected. The press of special construction is described. Further drying to 30% is accomplished during the cooling of the hot peat in the air and by passing it for 4 or 5 hr. through a tunnel drier heated by the waste heat from the power plant. About 25% of the heat energy of the peat is required for the steaming and the pressing operation. Such a press as

described costs about £2000 and will dry 60 tons of peat per day with a net yield of 15 tons at a cost of 17 s. 6 d. per ton. With a plant of 10 presses, the cost per ton would be 4s. 8d.

J. L. WILEY

Preliminary report on the manufacture of peat fuel. B. F. HAANEL. Can. Dept. Mines, *Summary Report* No. 574, 76-81(1922).—The Committee having in charge the government expts. to det. the feasibility of mfg. peat on a com. scale states (1) that the Anrep plant as it stands is in no sense com., (2) that the Moore plant under certain conditions can be employed commercially, (3) that the Anrep excavating element is the superior of the two and the logical one to employ, (4) that the Moore spreading system is far more efficient.

L. W. ROGGS

Lignites and peats in Italy. ALFREDO STROMBOLI. *Rass. min. met. chim.* 57, 107-8(1922).—A survey of the important lignite and peat deposits of Italy, estd. to be 300,000,000 tons, though only 1,020,000 tons of lignite were produced in 1921. Lignite contg. under 50% H₂O with a cal. power (dry) of 5000-6000 cal. amts. to 30,000,000 tons; xyloid and peaty lignites of 4000-5000 cal., (dry) giving 30-50% aq. NH₃ amts. to 163,000,000 tons; and peat with 30-5% H₂O amts. to 35,000,000 tons. There are 5 chief projects. All productions are in tons per yr. A 15,000 kw. station at Torre del Lago gasifies 100,000 tons of dry peat yielding (NH₄)₂SO₄ 5000 and tar 5000. At Pietrafitta a 15,000 kw. station gasifies 158,000 tons of lignite and gives (NH₄)₂SO₄ 2850 and tar 3000. At Mesio a station of 108,000,000 cal. capacity gasifies 30,000 tons of dry peat, yields 38,000,000 m.³ of gas and lime 2000, bricks 25,000,000, (NH₄)₂SO₄ 1700 and tar 1000. At Capalbio a 4,000 kw. station gasifies 3600 tons of dry peat and yields (NH₄)₂SO₄ 1850 and tar 1300. At Cagliari a station of 60,000,000 cal. capacity gasifies 12,000 tons of pitch lignite to produce 2500 tons of Portland cement. From a proposed 2,500,000 ton production of lignite there is available: (NH₄)₂SO₄ 50,000, crude tar 15,000, tar from the dist. 30,000, light oils 2,100, lubricants 10,000, heavy oils 6,600, paraffin 4,500, pitch 2,700, gas 300,000,000 m.³ C. C. DAVIS

The coloring constituents of montan wax. J. MARCUSSEN AND H. SMELKUS. *Chem.-Ztg.* 46, 701-2(1922).—The most exhaustive analysis to date of montan wax (A) is reported. By extn. of A with Et₂O, 73% insol. was left. Dild. of the ext. with an equal vol. of EtOH and cooling to -20° gave 18% wax of low m. p. In soln. 9% resin. remained *Et₂O-insol.* wax.—Saponified in C₆H₆ by alc. KOH, neutralized, evapd. to dryness, extd. with petr.-ether and with Me₂CO, 15% ext. was obtained. EtOH extd. most of the residue, but not the *potassium salt*, a shining brown-black mass, 10% by wt. of the A, sol. in 50% EtOH, benzine, C₆H₆, hot H₂O, insol. in 96% EtOH, Ac₂O and cold H₂O. With (EtCO)₂O the propionyl no. was 81. The *silver, iron, zinc and barium salts* were insol. in H₂O. The Ba salt contd. 7.85% Ba. This K salt gave the *oxy-acid* (B) a dark brown, easily pulverized solid, softening at 100° with no further change at 200°, almost insol. in EtOH, Et₂O, Me₂CO, HOAc and Ac₂O, sol. in C₆H₆, PhMe, CHCl₃, AmOH and warm benzine. On long standing it became insol. in C₆H₆, the sapon. no. was 94, acid no. 58; and I no. 13. It contd. 3.1% S as well as O. Alc. HCl did not esterify B, in distinction to montan- and carboeric acids (cf. C. A. 15, 1310). B was evidently identical with the oxy-acid of Graefe (cf. *Braunkohle* 1907, 222) and was a mixt. of products at various stages of oxidation. By long heating of the acid with AmOH and Na, the dark soln. became light, giving approx. 70% of a fatty acid which could be crystd. from EtOH. *Et₂O-sol. wax.*—A similar procedure to that for the Et₂O-insol. wax was followed. Six % of B or 1 % of the A was obtained. *Resin.*—Distn. of the solvent left a dark brown, brittle resin (C) sol. in Et₂O, C₆H₆, CHCl₃, and C₆H₅N, clear in thin layers, I no. 51, acid no. 16, sapon. no. 68, contg. 3.3% S. Let stand with cold concd. H₂SO₄, dild. with H₂O, filtered and washed with cold H₂O it gave a green compd., sol. in C₆H₆, CHCl₃ and C₆H₅N, contg. 4% S, yield 73%. Heated

with H_2O , H_2SO_4 was split off. By similar cold treatment but with subsequent heating, a black compd. was obtained, not wholly sol. in $\text{C}_6\text{H}_6\text{N}$, contg. 7.8% S, yield 83%. It could not be melted. C heated with fuming H_2SO_4 at 100° , and poured in H_2O , gave a black ppt. C treated with HNO_3 (d. 1.52), poured in H_2O , filtered, the residue dissolved and purified in Me_2CO gave the *nitro compound* (D), 107% by wt. of C, contg. 4.2% N, insol. in benzine and Et_2O , sol. in $(\text{CH}_2\text{Cl})_2\text{CH}(\text{OH})$, EtOH and CHCl_3 and with a dark color in alkalis, NH_4OH , and $\text{C}_6\text{H}_6\text{N}$. From these last solns. D was pptd. by mineral acids, BaCl_2 , AgNO_3 , $\text{Fe}_2(\text{SO}_4)_3$, etc. Besides the coloring constituents B and C, various grades of A contd. 1-18% finely divided lignite. C. C. DAVIS

Problems of heat economy in Germany. W. QUACK. *Z. anorg. Chem.* **35**, 621-5 (1922).—A general discussion which emphasizes various well known means of increasing the thermal economy of a power plant. There is an illustration of the application of the Ruth steam accumulator for equalizing the *discrepancies between steam production and steam consumption in a paper mill.* W. L. BADGER

Underfeed stokers burn low grade of coal. C. E. REESE. *Blast Furnace Steel Plant* **10**, 588-91 (1922).—Details are given of specially designed underfeed stokers for burning a low-grade coal at the boiler plant of the Twin City Rapid Transit Co., Minneapolis, Minn. The av. operating efficiency of the plant is about 70% at 350% of rating. J. L. WILEY

Flue gas diagrams. A. HALLBÄCK AND V. CHRISTIANSEN. *Teknisk. Tids.* **52**, *Uppl. A*, 801-6 (1922); cf. Ostwald, *C. A.* **14**, 2414.—This paper is based on recent German literature on the graphic representation of flue gas compn. The graphs (5) are constructed from analytical data of representative fuels. From the O_2 and CO_2 , the % of CO and "air factor" may be read off from the chart. A. R. ROSE

Limit of inflammability of vapors of the gasoline-alcohol system and a tertiary system with an alcohol and gasoline base. R. G. BOUSSU. *Compt. rend.* **175**, 30-2 (1922).—The characteristics of a motor fuel are: the limits of inflammability, ignition pressure, heat of combustion, and the rate of propagation of the flame. The variations of the lower limit of inflammability of ether (d. 0.720), alc. (d_{15} 0.810) and gasoline (0.725) were detd. The app. consisted of a cast Fe cylinder of 2300 cc. capacity immersed in

% ether.	$\theta = 50^\circ$.			$\theta = 90^\circ$.		
	Limit of inflammability.	$\frac{n}{N} + \frac{n'}{N'} + \frac{n''}{N''}$		Limit of inflammability.	$\frac{n}{N} + \frac{n'}{N'} + \frac{n''}{N''}$	
0	8.7%	1.00		6.4%	1.00	
20	7.0%	0.95		5.4%	0.97	
40	6.0%	0.94		4.8%	0.96	
60	5.5%	0.97		4.4%	0.96	
80	5.0%	0.98		4.1%	0.97	
100	4.6%	1.00		3.9%	1.00	

a water bath, a thermometer, stirring device and a thermoelec. couple attached to a galvanometer to det. the temp. of the inside walls and to control the explosion temp. The data given show that the LeChatelier formula for the limit of inflammability of a mixt. of 2 or more gases with air (n/N) + (n'/N') + (n''/N'') + ... = 1, where n, n', n'', \dots are the percentages of the various combustible gases in a mixt. which will just propagate flame, and N, N', N'', \dots are the limits of inflammability of the sep. gases, checks with data, with an error of less than 6%. For pure alc. the limit of inflammability was found to be: 20° 14.0%, 50° 11.4%, 90° 8.8%, 120° 6.7% and 150° 5.0%. For gasoline 20° 8.2%, 50° 7.5%, 90° 5.4%, 120° 3.9%, 150° 3.2%. Expts. with various amts. of ether added to a mixt. of gasoline and alc. whose vol. ratio was kept const., 3 to 2 vols., resp., showed deviations of less than 6% from the formula. In many cases, when ether was used, an odor of HCHO was noticed indicating incom-

plete combustion, and 2 sorts of combustion were noticed by the galvanometer deflections. The data are given in the accompanying table. **ACHILLE R. ALBOUZE**

Scientific utilization of the by-products of coal. **R. GIRARD.** *Rev. sci.* 60, 405-9 (1922).—An account of low-temp. carbonization with special reference to *coalite*.

J. L. WILEY

Boy's recording and integrating gas calorimeter. **ANON.** *Gas J.* 159, 25-30 (1922).—An illustrated supplement to *C. A.* 16, 2772.

J. L. WILEY

Carbonization of peat. **EDGAR STANSFIELD AND J. H. H. NICOLLS.** *Can. Dept. Mines, Summary Report No. 574*, 39-42(1922).—From 3 to 10 g. of briquetted peat contg. 25% moisture was weighed into a quartz crucible, this was placed in an iron retort, the cover was clamped and dry coal gas passed through the inlet tube to displace the air. The gas was then cut off and the retort immersed in a bath of oil or lead previously heated nearly to the desired temp. The progress of carbonization was watched by causing the evolved gas to bubble through water. In every case after the bath had been adjusted to the desired temp. it was held at that temp. for 30 min. The retort was then removed, was cooled rapidly and the crucible with its contents was weighed to det. loss. Conditions of work were standardized, especially the time factor. The following table shows the results of carbonization at different temps. and of analyses of the residues:

Temp. of carbonization.	Yield of residue %.	Cal. value per g.	Ash %.	Volatile matter %.	Fixed carbon %.
105	100.0	5350	6.0	62.3	31.7
250	86.0	6090	6.7	55.1	38.2
280	77.8	6400	7.3	49.9	42.8
350	63.3	6800	9.2	36.3	54.5
400	54.9	6840	10.7	26.7	62.6
450	49.7	6850	11.6	20.0	68.4
500	46.3	6910	12.5	15.8	71.7
550	44.0	7030	13.1	12.3	74.6
600	42.1	7090	13.6	9.7	76.7
650	40.6	6990	14.0	7.0	79.0
700	39.3	6900	14.4	5.6	80.0

As compared with lignites the percentage increase in calorific value at optimum temp. is much greater with peat. **L. W. RIGGS**

The Rincker system of complete gasification. **F. C. J. M. WIRTZ.** *Het Gas* 42, 71-6, 118-21, 139-42(1922); cf. *Buijs, C. A.* 15, 3385.—Extensive expts. were undertaken in the Utrecht gas works in order to det. the calorific balance of the process. The most important loss is caused by the heat of combustion of the blast gases (16.9%). 14.5% is lost by unburned C in ash and slags, 12.5% as heat content of the blast gases, 2.7% by radiation. **R. BRUTNER**

Determination of the degree of decomposition of water vapor in water-gas processes. **RICHARD LANT.** *Gas u. Wasserfach* 65, 257-61, 277-80(1922).—A new instrument for measuring the amt. of water vapor in water gas is described and the theoretical and mathematical bases therefor are discussed. The principle of the app. depends upon the local reduction in pressure caused by a baffle or constriction in a pipe through which gas is passing. If 2 constrictions are used, and the water vapor, which is thrown out of the gas between them, is removed, the additional loss in pressure is a measure of the vol. of water vapor. By means of this method water vapor detns. can be made to within an av. error of 1% of the % vol. of water vapor present when the barometer, he temp. of the cooled gases and the d. of the vapor free gases are known.

J. L. WILEY

Acetylene mantle burner tests. C. F. ROCKSTROH. *Gas Age-Record* 50, 178-9 (1922).—A mantle burner for C_2H_2 , called the Rock Light Burner, has been developed which insures complete combustion of either purified or crude C_2H_2 and will not carbonize under any operating pressure. After a 1600-hr. test, the c. p. of the mantle did not diminish. Burners, rated at $1/3$ and $1/4$ cu. ft., will give an av. of 111.6 candles per cu. ft. per hr. as compared with 20.36 candles by open flame burners rated at $1/3$ and $1/4$.

J. L. WILEY

Utilization of waste heat from water-gas production for generation of steam. F. STEDING. *Gas u. Wasserfach* 65, 716-21 (1922).—The heat losses from a generator plant are analyzed and various methods for recovering this waste heat are discussed. For each 100 m.³ of water gas, it is calcd. that there are 47,600 cal. available for production of 80 kg. of steam in waste heat boilers. The steam requirements for the operation are 70 kg. per 100 m.³ of gas. At the present cost of steam production, 15 pfg. per m.³, there is a clear saving of 13 pfg. after deduction of amortization, maintenance, etc., on the waste-heat plant.

J. L. WILEY

Removal of solid and liquid particles from gases. A. F. NESBIT. *Blast Furnace Steel Plant* 10, 637-41 (1922).—N. discusses the effects of solid and liquid particles on gases to be used for motive power. The multiple-unit combined elec. and centrifugal cleaner and the multiple unit centrifugal cleaner are described and illus. The centrifugal structure is adaptable as a steam separator, as an air dryer in compressor systems and as a collector of saw dust and dust from grinding and other processes. Applications are discussed and the advantages and disadvantages of both types are given.

W. H. BOYNTON

Chemical and physical bases of benzene washing. K. BUNTE and E. FREI. *Gas u. Wasserfach* 65, 273-7; *Am. Gas J.* 117, 673-6, 678-9 (1922).—Details of expts. are given for detg. the vapor pressure of benzene over its mixts. with washing oils at different temps. and concns. The soly. of benzene in washing oils follows phys. laws and is dependent upon the mean mol. wt. of these oils. The acid character (cresol content) of the oils has no chem. effect. Within the limits of the usual tech. concns. the vapor pressure of the benzene over the washing oils is proportional to the concn. of the benzene in the mixt. Rise of temp. reduces the soly.

J. L. WILEY

Substitutes for pine planer shavings as a carrying base for iron oxide in purifying material. S. J. MODZIKOWSKI. *Am. Gas Assoc. Monthly* 4, 439-42 (1922).—Detns. were made of the amt. of oxide that pine planer shavings, ground corn cobs, wood chips and chopped excelsior would retain per bushel. The prepn. and the mixing of materials were carried out as in practice. The efficiencies of the materials were in the order named, the resp. amts. of oxide retained being approx. 30, 20, 11 and 9 lb. per bushel. The 2 former mixts. were also tested for absorption of S, the fouling tests showing, resp., 5.566 and 2.486 lb. of S absorbed per bushel of purifying material.

J. L. WILEY

Report of experiments with a gas producer. TAMOTSU YASHORO. *J. Japn. Ceram. Assoc.* 361, 424-42 (1922).—Y. performed 83 expts. with a Dowson gas producer, which had a water-sealed Thwaite's ash-pit with a steam-blower. It consumed 18,700 lbs. of a Hokkaido coal per day. The most suitable temp. of the coke layer was 1000-1100°. When it was cooled below 800°, the gas was useless. The best gas was produced when steam and air were introduced into the blower in the ratio of 75.18 air: 24.82 steam (by vol.). The best results were obtained when the layers of coke and coal were 18-20" and 17-20" thick, resp.

S. KONDO

Fuel economy on gas-works boilers. T. W. ANDREWS. *Gas J.* 161, 82-5 (1923).—The problem of disposing of the surplus coke breeze at gas plants no longer exists. It can be very satisfactorily and efficiently burned under boilers for steam-raising purposes. It is quite possible, under normal working conditions, to obtain a steam evapn. of 6 lbs.

per lb. of fuel from and at 212° F. with coke breeze of 9500 B. t. u. per lb. No advantage is gained by screening comparable with the cost. Detailed directions are given for burning coke breeze under boilers.

J. L. WILEY

Continuous process of manufacture of gas suitable for filling balloons, heating, and lighting. Sealed note deposited 17,12,10. ARMAND LUTTRINGER. *Bull. soc. ind. Rouen* 50, 226-7(1922).—Solid, liquid, or gaseous hydrocarbons (e. g., tars and wastes from various org. industries such as synthetic camphor) are decomposed at a high temp. in a refractory tube filled with refractory material or with coke and placed in a chamber filled with incandescent coke. After some time a deposit of C is formed which is removed by blowing through steam and forming water gas. This is collected separately if the gas is to be used for balloons, but not if it is used for heating or lighting. **Report.** MARCEL LEMIRE. *Ibid* 226.—The process recalls that of Riché in which the products of wood distn. are decomposed into gaseous hydrocarbons by passing through wood charcoal heated to 900°. The originality of L.'s process lies in the automatic cleaning of the distn. tube.

A. P.-C.

Low-temperature distillation of fuels by the Moscicki process. R. MORITZ. *Chimie et industrie* 8, 1172-4(1922).—A brief description of the process, which consists essentially in heating to 450° the last portions of gases distd. from the fuel, and using these gases to carry heat through the mass of fuel to be distd. The equipment required, method of working, and advantages and applications of the method are outlined.

A. P.-C.

New gas meter of Swedish origin. B. TRANEUS. *Gas J.* 159, 35-6(1922).

J. L. WILEY

The ammonia products of the gas industry. D. STAVORINUS. *Het Gas* 42, 287-92(1922).—The patent literature which refers to the purification of $(\text{NH}_4)_2\text{SO}_4$ made from gas liquor is reviewed. Purification can be effected by (1) prep. a pure salt directly in the saturator, (2) washing the salt with NH_4OH after it has been drawn up by a sieve, (3) treating the salt with gaseous NH_3 , (4) mixing the salt with a neutral solid substance. The first and the last methods have no great importance; the second is usually employed. Small quantities of pyridine salts will render $(\text{NH}_4)_2\text{SO}_4$ hygroscopic.

R. BEUTNER

New tar-dehydrating plant. A. W. WARNER. *Am. Gas Assoc. Monthly* 4, 437-8 (1922).—The Philadelphia Suburban Gas & Elec. Co. has put into operation a continuous dehydrating unit for removing water from coal gas tar. The app. (shown in diag.) consists of a mixing tank, a steam-jacketed engine-driven pump, a steam-coil heat exchanger, and $\frac{3}{4}$ in. open end pipes feeding into a dehydrating tank. Tar flows continuously into the mixing tank from an overhead wet tar tank provided with a const. flow device, and is then pumped through the heating system into the dehydrating tank from whence the dry tar overflows into a storage tank, the vapors being taken off at the top of the dehydrating tank and condensed tar of any degree of dryness can be obtained. The app. can extract 40 gal. of liquor from 200 gal. of wet tar in 1 hr. without heating beyond 220° F. and with no frothing. The pump circulates about 50 gal. of hot tar per min.

J. L. WILEY

Volume loss by light oil removal. F. HENRY AND N. F. PRINCE. *Gas Age-Record* 50, 79-80(1922).—Expts. carried out at Rochester, N. Y. show that the loss in gas vol. due to light oil removal varies between 0.64 and 2.14%. Exptl. details are given.

J. L. WILEY

Disposal of spent liquor. T. L. BAILEY. *Gas J.* 159, 213-4(1922).—A supplement to the Alkali Inspector's Report for 1921. It contains matter, mostly historical, in connection with disposal of spent liquor effluents from NH_3 stills under the headings of admission to sewers, utilization at the works, chem. treatment, bacterial treatment on filter beds, and special processes.

J. L. WILEY

Chemistry of the coking process. Preparation of high melting point bitumen. FRIEDRICH LIERG. *Am. Gas J.* 118, 63-6, 74-7(1923).—Translation of *C. A.* 16, 3194. J. L. WILEY

New coke ovens use highly volatile coals. H. J. GIFFORD. *Am. Gas J.* 117, 45-8(1922).—The operation of the Roberts ovens at St. Louis is described. J. L. W.

Physical and chemical bases of dry coke quenching. EITNER. *Gas u. Wasserfach* 65, 732-4(1922).—The coke enters the cooling chamber at a temp. of about 950° and leaves it at 250°. The amt. of heat is thus about 332,000 cal. per ton of coke, of which 74.7% is available for steam production in the waste-heat boiler, 15.9% remains in the coke, and 9.4% escapes by radiation or otherwise. The av. initial gas temp. of 750° is reduced to 200° during the cooling period by contact with the boiler. The heat value of the gas is dependent not only upon its temp. but also on its heat capacity which varies with its content in CO₂. This amts. on the av. to 13.5%. Therefore its heat value at 750° per m.³ is 262 cal. and at 200°, 66 cal. For each ton of coke cooled per hr., 1265 m.³ of gas must be circulated in order to transfer this 196 cal. of heat from the gas to the boiler water. The amt. of air admitted during the charging or discharging of the chamber is so small that no trouble is experienced from combustion of the coke. It is calcd. that only 0.406 m.³ of air is admitted, capable of consuming 0.058 kg. of coke. Likewise leakage of air and gas is of no account owing to the air-tight condition of the chamber. Nor does there appear, under normal operation, to be any danger from explosion. The av. gas compn., immediately after charging, is as follows: CO₂ 114%, O₂ 0.6, CO 15.4, N₂ 72.6. J. L. WILEY

Dry coke quenching by the Sulzer process. KUCKUK. *Gas u. Wasserfach* 65, 729-32(1922); cf. *C. A.* 15, 2540; 16, 821 and preceding abstr.—K. discusses the economic phases of dry coke quenching and gives some operating results. J. L. W.

Report of Alkali Works' Inspector (BAILEY) 18. Report on the manufacture of industrial alcohol from Hawaiian molasses (McCLUREY, AGER) 16.

BACON, R. F. AND HAMOR, W. A.: **American Fuels.** Vol. I & II. London: McGraw-Hill Publishing Co., Ltd. 628 pp. & 629 pp. 60s. Reviewed in *J. Soc. Chem. Ind.* 41, 544R(1922).

BOOTH, WM. H.: **Liquid Fuel and its Apparatus.** 2nd Ed. New York: E. P. Dutton & Co. 308 pp. \$4. Reviewed in *Mech. Eng.* 44, 776(1922).

SINNATT, F. S., GROUNDS, A., STERN, H., BAYLEY, F., BARASH, M., HARRISON, W., McCULLOCH, A., AND CRAVEN, MAY B.: **Coal and Allied Subjects.** London: H. F. & G. Witherby, 326 High Holborn, W. C. 205 pp. 15s. Reviewed in *Chem. News* 125, 336(1922).

WEYMAN, G.: **Modern Gasworks Chemistry.** London: Benn Bros. 184 pp. 25s. Reviewed in *Engineering* 114, 780(1922).

Fuel. H. J. FRANKLIN and J. PETTINGALL. *Brit.* 187,351, July 30, 1921. A compn. fuel which is molded into block form is made up of 10 parts by wt. of asphalt or pitch, 800 parts of fuel oil, 25 parts of shale, and 45 parts of coal or coke, with or without 160 parts of tar, and 20 parts of peat impregnated with fuel oil. The shale and coal are finely ground and stirred in a mixing vessel into which steam is injected. Finely divided peat impregnated with oil may be added. The asphalt and sometimes tar, and fuel oil are heated in a sep. vessel and the mixt. when liquid is combined with the shale, etc., the incorporated mass being molded on cooling.

Liquid fuels. F. DE M. ACCIOLY. *Brit.* 187,640, April 20, 1921. Alc. liquids for use as fuels for internal-combustion engines, lamps, etc., are prepd. by distn. of fer-

mented saccharine juices or of alc. in the presence of enriching compds. Saccharine juices from sugar cane, oranges, cashew, manioc, beetroot, or watermelons, or solns. of molasses or raw sugar, are fermented by addn. of a mixt. of yeast, tannic acid, neutral K tartrate and H_2SO_4 . A compn. consisting of the liquid obtained by boiling orange peel in H_2O , Stockholm tar, coal tar, or petroleum tar and naphthalene is added, and the mixt. is again distd. If alc. is used in place of the fermented juices, a second compn. of Stockholm tar, coal tar, or petroleum tar dissolved in H_2SO_4 and mixed with alc. is added prior to the first distn. A suitable construction is specified.

Hydrogenating aromatic hydrocarbons to form motor fuel. A. S. RAMAGE. U. S. 1,439,976, Dec. 26. Vapors of aromatic hydrocarbons such as C_6H_6 , toluene or xylenes together with steam and vapors of non-aromatic hydrocarbons, *e. g.*, mixed hydrocarbons from coal tar, are brought into contact with FeO at a temp. of about 550° .

Motor fuel. H. R. GILES. Brit. 187,327, July 18, 1921. A fuel for internal-combustion engines comprises a mixt. of ether, alc., and a volatile vegetable oil such as rosin oil or oil of turpentine, with or without a small amt. of $NaOH$. The preferred proportions are 36.75 parts by vol. of alc., 62 parts of ether, 1 part of rosin oil, and 0.25 parts of a satd soln. of $NaOH$ in alc. "Commercial" ether may be used in slightly larger proportion. The fuel is miscible with lubricating oil and thus is suitable for two-stroke engines.

Motor fuel. F. E. LICHTENTHALER. Brit. 187,051, July 27, 1921. Alc.-ether mixts. suitable for use as motor fuels are produced by generating ether vapor, preferably from alc., and condensing it by absorption in alc. Alc. is treated with H_2SO_4 in a generator, and the ether vapors are neutralized and concd. in a scrubber and a fractionating column fitted with a reflux condenser. The vapors then enter a condenser where partial condensation occurs, even when only warm ($80-85^\circ F.$) condensing H_2O is available; the uncondensed vapors are led into a tower where they are absorbed in water-cooled alc. The mixt. from the tower is mixed with the liquid ether from the condenser. Where the condensing water is sufficiently cold, preliminary partial condensation is omitted, and the ether vapor is directly condensed and absorbed in cooled alc.

Motor fuel. S. W. BLAKE. Brit. 187,335, July 19, 1921. The method of producing an alc. fuel described in 178,498 (*C. A.* 16, 3384) is applied to no monohydric alcs., other than com. alc., such as amyl, butyl, and propyl alcs. The alcs. preferably contain up to 10% of H_2O , and 5-40%, or more, of acetone is added. The pressure is preferably from 10 to 40 lb. per sq. in., depending on the amt. of C_2H_2 to be absorbed. The CaO in soln. or suspension in fuels of this type is removed by chem. means, such as by treating the fuel with NH_3 and passing in CO_2 , or by the addn. of powd. NH_4CO_3 . A suitable lubricant may be added.

Carbonizing coal. SOC. LYONNAISE DES EAUX ET DE L'ECLAIRAGE. Brit. 186,927, Oct. 4, 1922. Powd. coal is coked by being projected into a heated chamber in which an atm. of H is maintained. The powd. coal from a hopper is delivered by a centrifugal projector into a chamber, the walls of which are heated to redness. A gas contg. H is supplied by a conduit and may be preheated by passage through red-hot coke or a heat regenerator. A coke mass is formed retaining certain binding constituents which are necessary for the agglomeration of the coke which is assisted by the compression due to the impact of the coke particles. The gas generated escapes by a pipe.

Purifying fuel gas. E. V. ESPENHAHN. U. S. 1,440,977, Jan. 2. Any ordinary fuel gas is passed through a soln. of $NaHCO_3$ and Na_2CO_3 to absorb impurities; the soln. is heated to remove absorbed impurities and regenerate it and is then used for purifying a further quantity of gas.

Gas. E. BRODSKY. Brit. 186,724, July 7, 1921. Wood, coal, etc., is distd. in a retort forming part of a portable plant, the condensates are collected and the gases are

passed through a condenser and scrubber and are used partly or entirely for heating the retort; a residue of charcoal or coke remains. A suitable construction is specified.

Water gas. COMMANDITAIRE VENNOOTSCHAP VAN KOOPHANDEL ONDER DE FIRMA "GASWERKEN" TE LEIDSCHENDAM, GEMEENTE VEUR. Holl. 7399, May 24, 1922. Brit. 25277 (1898) describes an app. with which water gas is produced in an unlined generator surrounded by a water jacket in which steam is produced. A similar app. is now described with the addition of an attachment for an alternating air and gas supply which keeps the pressure in the water jacket more or less constant; heat for the production of steam is supplied from the central coke-core.

Control device for pilot lights of water-gas apparatus. T. S. BARLOW. U. S. 1,441,905, Jan. 9. A device is provided for regulating the flow of gas to the burner in accordance with the degree of opening or closure of the stack valve.

Gas producer. R. DAAE. U. S. 1,441,217, Jan. 9. Structural features, especially relating to mounting and operation of pokers at the surface of the fuel bed.

Gas producer. W. B. CHAPMAN. U. S. 1,441,330, Jan. 9. The pat. relates to mechanism for mounting and rotating the fuel agitator.

Oil-gas producer. A. FRICKER. U. S. 1,441,272, Jan. 9.

Supplying moisture to gas producers. H. F. SMITH. U. S. 1,442,100, Jan. 16. H_2O is sprayed into the air passing to the generating chamber of the producer and the quantity of spray is regulated by a valve controlled by heat from a gas burner or absorption app. in accordance with the compn. of the gas produced, so that uniform operation is facilitated. Cf. C. A. 16, 824.

Fuel-feeding device for gas producers. J. F. ROGERS. U. S. 1,439,912, Dec. 26.

Producer furnace for heating aluminium chloride stills. G. D. WHITE. U. S. 1,440,857, Jan. 2.

Ammonium sulfate. W. C. HOLMES & Co., LTD., W. G. ADAMS TAR & AMMONIA PRODUCTS WORKS and C. COOPER. Brit. 187,035, July 16, 1921. $(NH_4)_2SO_4$ is dried and neutralized in one operation by mechanically conveying the crude salt through a chamber or casing through which a current of NH_3 gas and heated air flows in the reverse direction to the salt. A suitable construction is specified. Cf. 108,098 (C. A. 11, 2960).

Coking processes. S. R. ILLINGWORTH. Brit. 187,328, July 18, 1921. Coal which has a volatile content of 14–20% at 900° , and in which the major portion of the resinic matter decomposes at a temp. of from about 350° to 400° with the evolution of only a small quantity of volatile matter, is heated to a temp. not exceeding 600° to obtain a smokeless fuel. If desired, this fuel may be heated above 600° , say to 900° , to produce a metallurgical coke. The coal may be heated in thin layers, but if thicker layers are to be used a blend should be made. Cf. 175,888 (C. A. 16, 2217) and C. A. 17, 336.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Some new nitrogen compounds from Baku crude petroleum. EWALD PYHALÄ. *Chem.-Ztg.* 46, 953 (1922).—The substance obtained by dilg. with H_2O the acid sludge from kerosene agitators was distd. from a glass flask with superheated steam. Oil was introduced continuously from a scpg. funnel. The distillate was shaken out with H_2SO_4 (not too concd.). A soln. of NaOH was introduced from a scpg. funnel into the acid ext. contained in a flask provided with a Liebig condenser. The temp. rise due to the process of neutralization was sufficient to cause the lower boiling constituents to distil. Combustible gas was evolved, also, and was passed through a cooled concd. soln. of NaOH. The gas escaping from the train of absorption bottles produced white

fumes when passed over a glass rod moistened with concd. HCl. In the receiver and also in the absorption bottles, a light yellow distillate collected. The distn. was continued after complete neutralization of the H_2SO_4 by application of a gas flame. The total distillate, a light yellow oil, passed over principally between 75° and 80° . The following results were obtained by treating the fractions with PtCl_4 . Fraction from 75° to 120° gave a brownish red ppt. which is sol. in CHCl_3 (yellow soln.). A yellowish brown ppt., obtained from the fraction b. 120 – 147° , dissolved in CHCl_3 to form a brown soln. The fraction b. 147 – 187° formed a dark brown ppt. having a violet tinge. This ppt. formed a carmine-red soln. with CHCl_3 . The residue b. above 187° behaved similarly to the last distillate, but the ppt. had a stronger violet tinge. All of the ppts. are tarry and easily sol. in CHCl_3 . All of the fractions contain constituents sol. in a 5–6° Bé. soln. of NaOH, and all fume in the presence of a rod moistened with HCl. A soln. of PdCl_2 gave with the fractions ppts. having colors ranging from pale yellow through orange to brown. The residue gave a cherry-red ppt. having a violet tinge. The solns. made with CHCl_3 varied from yellowish brown to black for ppts. from the distillates. The ppt. from the residue gave a dark violet soln. with CHCl_3 . The compds. are obviously amines which were not present in the crude petroleum. It is probable that they were derived from carboxylic acid amides, existing in the crude petroleum, by the oxidizing action of the H_2SO_4 used in refining, and by the subsequent distn. with superheated steam. The original constituents were probably formed by the anhydrous reaction between the carboxylic acids and NH_3 . W. F. FARAGHER

The desulfurization of crude-oil distillates. H. I. WATERMAN AND D. W. SISSINGH. *Chem. Weekblad* 19, 489–92(1922).—Mexican mineral oil distillates are treated either with concd. H_2SO_4 and NaOH or with sodium plumbite and flowers of sulfur (cf. Ellis and Meigs, Gasoline and Other Motor Fuels, C. A. 15, 2173). The latter treatment leads to an increase of the S content; by redistn. the S is again eliminated and large quantities of H_2S are produced. This "Doctor treatment" is, therefore, in its present form not applicable to Mexican oil distillates. The treatment with concd. H_2SO_4 and NaOH diminishes the S content by 50–60%. R. BEUTNER

Christman process is now installed on seven Mid-Continent plants. J. C. CHATFIELD. *Nat. Petroleum News* 14, No. 46, 23–4(1922).—The Christman process (U. S. pat. 1,243,384) is similar in principle to other tower processes in use. The construction of the Christman tower or dome is different from any other type and is claimed to increase the gasoline yield from 2 to 10% on all installations and tests as yet made. A dome for each still is 6 ft. in diam. and 12 ft. high. The top and bottom are dished outward. Two pans are suspended in each dome; the lower is 5 ft. $10\frac{3}{4}$ in. in diam. and 3 ft. $1\frac{1}{2}$ in. deep, while the upper pan has the same diam. but is 5 ft. $1\frac{1}{2}$ in. deep, thus allowing an open space of $\frac{5}{8}$ in. between the pan and shell of the dome. A 2-in. pipe from the center of the upper pan provides drainage to the second pan, which has a back trap line running to the same still or still head as desired. A second back trap line leaves the bottom of the dome having sep. connections with the battery of stills. A baffle plate carrying 630 holes $\frac{1}{2}$ in. in diam. within a circle 3 ft. 2 in. in diam. is placed between the two pans. The combined area of the perforations is equal to that of the 12-in. vapor inlet near the bottom of the dome. The process requires more expert men in its operation, but material coming from the condenser box is so closely cut that no re-running is necessary. A yield of $29\frac{1}{2}\%$ of 64–66° Bé., 375 end-point gasoline has been obtained from Burkburnett crude. D. F. BROWN

Types of oil distillation. ANON. *Petroleum Age* 11, No. 3, 16–7, 67, 93(1923).—A comparison of steam, vacuum and ordinary distn. methods. Towers for fractionation increase the efficiency of the distn. process and are more effective if used in series of 2 or 3. Batch vs. continuous stills are discussed and the relative merits of each brought out.

D. F. BROWN

The extraction of gasoline from natural gas. G. A. BURRELL. *J. Soc. Chem. Ind.* **41**, 524-7R, 540-53R(1922).—Production of gasoline from natural gas amts. to 8% of total production. Natural-gas gasoline is added to refinery gasoline to increase the volatility of the latter. Dry natural gas contains 0.5 gal. gasoline per 1000 cu. ft. Casing head gas contains up to 10-15 gal. per 1000 cu. ft. The compression method is generally used for the extn. of gasoline from casing-head gas. The absorption method is usually applied to dry natural gas. The gasoline is sepd. from oil by a steam distn. Efficiently managed compression plants have small absorption units to treat their residual gases, as high pressures do not entirely condense the gasoline. This remaining gasoline is absorbed in naphtha. The heating value of dry natural gas is lowered about 2% by extg. the gasoline. The loss is somewhat greater for casing-head gas. A third method for the extn. of gasoline from natural gas is based upon the adsorptive power of activated charcoal. The activated charcoal, 8-14 mesh, is placed in 3 absorbers, 6 ft. X 5 ft. for a plant producing 1000 gal. gasoline per day. The natural gas is passed through one of the absorbers until the charcoal has become satd. with gasoline up to 15% of its wt. The gas is then turned into another absorber and the gasoline driven out of the first absorber with steam. At low pressures, 2-5 lbs. per sq. in., the absorbent action of charcoal is very efficient. Information in regard to plant design and cost is given for the three processes described.

C. T. WHITE

Absorption plant at Casper (gasoline from gas). ANON. *Nat. Petr. News* **10**, No. 5, 37-8(1923).

D. F. BROWN

Decolorization by absorption during filtration. F. N. WILLIAMS. *Refiner & Nat. Gasoline Mfr.* **1**, No. 4, 7-8(1922).—The temp. of filtration and the size of grain are of great importance as well as the kind of filtering material selected. Heat is generally evolved during active absorption. Since the temp. of filtration is of importance, the following are recommended: wax, 150° F.; heavy viscous engine oils, 120-130° F. and non-viscous oils at 90° F. When the quality of the filtered material has reached a predctd. color, the feed is stopped, the filter permitted to drain, the filter washed with warm naphtha until practically colorless and then steamed to remove the naphtha. The bottom of the filter is opened and the filtering medium removed and revived. In the case of fuller's earth ignition is made at 1000-1200° F. ARTHUR L. DAVIS

The physico-chemical significance of flash point temperatures. W. R. ORMANDY. *Petroleum Times* **9**, 87-9(1923).—Data are given for flash points on different liquids both under atm. and increased pressures.

D. F. BROWN

Oil shale. A resumé for 1922. V. C. ALDERSON. *Railroad Redbook* **40**, No. 1, 9-22(1923).

D. F. BROWN

Oil shales. III. The distribution of oil shales in the eastern part of European Russia. L. VON ZUR MÜHLEN. *Petroleum Z.* **18**, 1477-82(1922).—A general description of these deposits, with analyses. The principal deposits lie along the Volga and between it and the Ural rivers, the richest and most extensive being the Steppes of Obschi Syrt. Economic conditions bearing on development are discussed. A short bibliography is appended.

D. F. BROWN

The torbanites of Nova Scotia. D. T. DAY. *Oil Eng. and Finance* **3**, 37-42(1923).—A general discussion of the shale deposits of this region. Oil obtainable from these shales amounts to 38-60 gals. per ton and the $(\text{NH}_4)_2\text{SO}_4$ 71-80 lbs. per ton. A representative sample gave (in %): oil 17.7, water 3.3, gas 3.0, C 8.4 and ash 67.6. The oil had a sp. gr. of 0.852. Distn. tests were compared with Mexican crude petroleum.

D. F. BROWN

Oil shale unsaturates. C. W. BOTKIN AND R. W. BOYD. *Petroleum Age* **11**, No. 3, 56-62(1923); cf. *C. A.* **17**, 465, 629.—The decompn. attending distn. of oil shales lowers the % of N in the fractions but does not materially change the I nos.

The I nos. of the acid-sol. oil decrease very rapidly with increase in gravity and b. p. The decompn. increases the N content of the acid-sol. oil and causes a large increase in the I no. of the light fractions which contain the highest amt. of "new" saturates. The I no. of the acid-sol. portion of the heavy fractions are similar to olefins of equal b. p. The light unsatd. acid-sol. oils from shale contain over 1% of N. It is suggested that compds. similar to these may make up the gum-forming constituent of gasolines and that a large ratio of I no. to H_2SO_4 absorption no. may serve as an indication of the presence of these constituents.

D. F. BROWN

The petroleum industry in Poland. S. BARTOSZEWICZ. *Petroleum Times* 9, 79-82(1923).—A description of the various producing regions together with production figures and quality of the crude for each. A map is given.

D. F. BROWN

The chemistry of petrolatum. J. D. GILL. *Petroleum Age* 10, No. 8, 80-1(1922).—Petroleum products may be classified in groups as follows:

(1)	Sp. gr.	B.-p. range ° F.	Approx. %C.	Chem. compn %H.
Pentane.....	0.632	80-115	83.3	16.7
88° gasoline.....	0.645	90-170	83.5	16.5
76° gasoline.....	0.682	100-300	83.7	16.3
68-70° gasoline.....	0.705	110-320	84.0	16.0
66° ext. naphtha.....	0.716	110-340	84.4	15.9
Motor gasoline.....	0.738	130-420	84.4	15.6
Paint-makers naph.....	0.759	185-400	84.6	15.4
Safety solvent.....	0.780	200-440	84.7	15.3
(2) Kerosenes				
	0.796	300-600	84.9	15.1
	0.808	350-590	85.2	14.8
	0.812	340-590	85.4	14.6
	0.816	330-600	85.6	14.4

(3) Gas oil and other non-viscous, pale, lubricating oils

(4) Waxes.

Factors detg. the usefulness and the effect of chem. reagents are described. D. F. B.

Composition of paraffin wax. III. FRANCIS FRANCIS, C. M. WATKINS AND R. W. WALLINGTON. *J. Chem. Soc.* 121, 2804-10(1922); cf. *C. A.* 16, 2301.—An account is given of the air oxidation of the 7 constant-boiling fractions (constituting 80% of the wax) at 100°. In all cases CO_2 and HCO_2H were produced and their detn. indicated that the amts. of C in both these substances correspond closely in each case with the oxidation of 1 g.-atom of C per 1 g.-mol. of hydrocarbon. The results are given in a table, which shows the mol. wt. of the original and oxidized product, the acid value of the latter, the % of α - and β -acids, of γ -acids, m. p. and acid value, the % of acids as esters or anhydrides, m. p., % of alcohols, % of unoxidized hydrocarbons, mol. wt., m. p. and mixed m. p. with original material. The unoxidized residue is identical with the original material (mixed m. p., mol. wt.) which is considered as strong evidence that the fractions of const. b. p. isolated from paraffin wax are pure hydrocarbons and not mixts. No attempt to identify any of the oxidation products is reported.

C. J. WEST

Colombian oil fields (HUNTLEY, MASON) 8. A petroleum field intelligently developed (PAPARELLA) 8. Purification of MeOH by means of NaClO (MENZIES) 10.

HANDEL, JEAN A.: *Recherche et exploitation du pétrole.* Paris: Dunod. 275 pp. Fr. 16.

MARTIN, A.: *Le pétrole. Son origine, sa composition, sa recherche.* Paris: Felix Alcan. Fr. 6.

Destructive distillation of petroleum fractions. U. S. JENKINS and S. SCHWARTZ. U. S. 1,440,996, Jan. 2. A petroleum fraction such as a gas oil of 34° Bé. is supplied to a series of pressure stills and overhead pressure distillate is removed until the gravity of the remaining oil is increased in the different stills to materially and successively greater amts. Fresh oil is added to the first still to maintain its contents of approx. const. sp. gr. and oil is successively passed from each still to the next to maintain the same approx. increased sp. gr. in each still after once established, residual oil being withdrawn from the last still of the series.

Cracking petroleum oils. R. F. BACON and B. T. BROOKS. U. S. 1,439,683, Dec. 26. A heavy distillate of mixed base petroleum such as that from Oklahoma crude oil, which has a sp. gr. above 0.860 and is substantially free from lower b. p. solar oil of lower sp. gr. and from heavy base constituents, is subjected to a combined cracking and distg. operation at a pressure of 60-300 lbs. per sq. in. and a temp. of 300-500° to obtain a fuel for internal-combustion engines.

Cracking oils. F. TINKER. Brit. 188,058, July 29, 1921. See U. S. 1,393,184 (C. A. 16, 488).

Retorts in series for cracking petroleum oils under pressure. C. P. DUBBS. U. S. 1,440,772, Jan. 2. Preheated oil is fed successively through connected retorts each of which is heated to cracking temp., vapors are passed through successive retorts and then to a condenser under pressure. The reflux from a dephlegmator is passed again through the retorts for retreatment.

Electro-osmotic separation of water from petroleum oils. W. MEREDITH. U. S. 1,440,835, Jan. 2. A d. c. is passed between a body of H₂O and aq. petroleum emulsion, sepd. by a porous diaphragm which may be formed of leather, unglazed porcelain or wood.

Apparatus for dehydrating and cleaning petroleum oils. R. G. JONES. U. S. 1,440,832, Jan. 2. The oil, naturally emulsified with H₂O, is heated, washed and subjected to gravity sepn.

Electric apparatus for dehydrating petroleum oils. F. W. HARRIS. U. S. 1,440,828, Jan. 2.

Electric apparatus for dehydrating petroleum oils. W. O. EDDY. U. S. 1,440,774-5-6, Jan. 2.

Scrapers for cleaning the interior of petroleum stills. C. S. BROWN. U. S. 1,441,058, Jan. 2.

Halogenated hydrocarbon mixtures. C. ELLIS and A. A. WELLS. U. S. 1,440,976, Jan. 2. An acid ext. such as is obtained by the treatment of gasoline contg. olefins with strong H₂SO₄ is subjected to the action of a halogenating agent such as Cl or bleaching powder to obtain chlorinated hydrocarbons or chlorohydrins.

Hydrogenating oils. G. F. FORWOOD. U. S. 1,440,286, Dec. 26. Coal oil, shale oil, petroleum, lignite oil or a similar oil is atomized under pressure and mixed with steam and the mixt. is passed through charcoal heated to about 570° to effect decompn. of steam and hydrogenation of cracked products of the oil.

Dehydrating oil in storage tanks. O. C. GATRELL. U. S. 1,440,352, Dec. 26. Port. cement and Ca(OH)₂ in powd. form are added to the oil, which is heated and agitated.

Desulfurizing oils. W. R. WALKEY and A. F. BARGATE. Brit. 186,738, July 18, 1921. Petroleum, etc., are desulfurized by vaporizing the oil to convert the S into H₂S, and then treating the vapors with H₂O or steam and a gaseous oxidizing agent such as

Cl or SO_2 , preferably under the action of a magnetic field. The vaporized oil, steam, and oxidizing agent are led into a chamber, packed with fire-brick, pumice, etc., and surrounded by an elec. coil. The chamber is heated to $300\text{--}400^\circ$. In an example, the oil is vaporized, and the contained vol. of H_2S is detd. An equal vol. of Cl or SO_2 and 5 vol. of steam at 240°F . are then admitted.

Desulfurizing petroleum. A. E. DUNSTAN and F. B. MEADHURST. Brit. 186,955, May 9, 1921. In desulfurizing petroleum or petroleum distillates in the liquid state by adsorptive treatment with a dehydrated natural or artificial inorg. gel, the desulfurizing agent is used when freshly ignited and while still warm. Varieties of fuller's earth such as Floridin, or bauxite, or metallic hydroxides of a colloidal character, such as Fe and Al hydroxides, may be used. The oil is mixed with the adsorptive substance or filtered through it. Means such as a steam-jacket may be provided to maintain the oil and adsorptive substance warm during contact. In treating benzine, 4 lb. of Floridin or 9 lbs. of bauxite per gal. are used.

Gasoline from natural gas by absorption. J. B. GARNER and S. C. PRESTON. U. S. 1,437,101-2, Nov. 28. Natural gas is passed successively through 2 bodies of a gasoline-absorbing menstruum, preferably a liquid petroleum hydrocarbon material of $28\text{--}55^\circ\text{Bé}$. The first body of absorbent may be sprayed into the top of an absorption chamber filled with fragments of inert solid material such as coke, broken stone or steel turnings. The second body of menstruum may be maintained in the form of a pool through which the gas passes or it may also be sprayed into an absorption chamber or tower countercurrentwise to the gas to be treated. A single absorption tower also may be used, in which case the gas is passed upwardly through the tower; fresh absorbing oil is sprayed into the top of the tower and oil-gasoline soln. from a pool in the base of the tower is pumped back into a zone mid-way of the tower's height. The relative rates of flow of gas and absorbent are so controlled that the menstruum through which the gas last passes undergoes a rise in Bé . of only about 1° . The gas may be treated under any desired pressure, e. g., 20 lbs. per sq. in. or less, and the manner of contact of gas and absorbent facilitates good recoveries of gasoline at relatively low pressures.

Apparatus for recovering gasoline from natural gas by absorption in oil and distillation. E. A. STARKE. U. S. 1,439,921, Dec. 26.

Treating oil-bearing shale. H. R. STRAIGHT. U. S. 1,441,542, Jan. 9. Shale is first heated to remove the more volatile products and limited amts. of O are then supplied to the interior of the mass of heated shale while the latter is agitated by rotating an inclined retort in which it is held. Further distn. is effected by increased temp. resulting from combustion of a portion of the shale itself.

Vertical retort adapted for distilling oil shale. L. SIMPSON. U. S. 1,441,380, Jan. 9.

Asphalts, etc. J. H. YOUNG and H. H. ROBERTSON Co. Brit. 186,861, Dec. 6, 1921. Bituminous materials, such as asphalt, tar and pitch, are fireproofed by an admixt. of a halogen substitution-product of naphthalene, preferably chloronaphthalene. The solid, highly chlorinated compds. are most effective, an addn. of 30% of these being sufficient.

Purifying pyroligneous acid and other liquids. T. J. BREWSTER. Brit. 187,603, Oct. 16, 1922. HOAc is extd. from crude pyroligneous acid by treatment with a volatile solvent, which is immiscible with H_2O and of materially different sp. gr., such as ether, $\text{C}_2\text{H}_5\text{Cl}$, CHCl_3 , $\text{C}_2\text{H}_5\text{Cl}$ and $\text{C}_6\text{H}_5\text{Br}$. The tarry substances may be first removed by distn., but preferably the vapors resulting from the distn. of cellulosic material are passed through a scrubber maintained at a temp. above the b. p. of H_2O and down which high-boiling oils or tar trickle. MeOH may then be substantially removed by distn. A suitable construction is specified.

Reducing bituminous material to dust form. C. C. BANCROFT. U. S. 1,441,904, Jan. 9. Bituminous material such as asphalt is heated in a closed vessel and air is passed under pressure into the material to aerate it and assist in forcing it out through an exit pipe. On its egress from the latter into the air it is atomized with a further quantity of air under pressure, finely to subdivide the particles before they undergo solidification.

23—CELLULOSE AND PAPER

CLARENCE J. WEST

Stability and stabilization of cellulose nitrate for celluloid. KATSUMOTO ATSUKI. *J. Coll. Eng., Tokyo Imp. Univ.* 11, 201-52(1922).—The main impurity which causes the instability of cellulose nitrate for celluloid is H_2SO_4 fixed as esters and an adsorption compd. Oxy- and hydrocelluloses do not seem to be the direct cause of instability but evidently form a subordinate cause because of their greater affinity for H_2SO_4 . A nitrating bath contg. only HNO_3 and H_2O will give a nitrate which is easily stabilized but it has a low viscosity and is not suitable for celluloid. The best conditions for nitration (yielding a product of high viscosity and low H_2SO_4 content) consist in using normal cotton cellulose and a bath of equal parts of H_2SO_4 and HNO_3 (by wt.) together with 18-20% H_2O ; the nitration is conducted at 25° for 1 hr., with 50-100 parts of acid to 1 part dry cellulose. The stabilization of the nitrate for celluloid must be carried out so as to eliminate the fixed H_2SO_4 without decreasing the viscosity. Acid boiling proposed by Robertson is too drastic. Hot-water washing is not effective. The most suitable method of purification is to use a salt soln., as $\text{Pb}(\text{NO}_3)_2$, by means of which the H_2SO_4 is ppt. as an insol. salt. The acidity produced by the HNO_3 formed in the reaction is sufficient to promote the further sapon. of the fixed H_2SO_4 esters. The PbSO_4 which is formed is retained by the nitrate as an adsorption compd. and gives an opaque appearance to the celluloid. This must be removed by washing with hot dil. HNO_3 and the $\text{Pb}(\text{NO}_3)_2$ and H_2SO_4 then removed by thorough washing. Camphor exerts a stabilizing action on celluloid but the influence of the nitrate is more important than that of the camphor and the stability of the celluloid is proportional to that of the nitrate used. The lowest limit of stability tests allowable as the material of celluloid may be taken as 10 min. at 80° by Abel heat test and 180° by ignition point detn.

C. J. WEST

Solubility and viscosity of cellulose nitrate for celluloid. K. ATSUKI. *J. Coll. Eng., Tokyo Imp. Univ.* 13, 1-39(1922); cf. preceding abstr.—The soly. of cellulose nitrate in alc. camphor (95% EtOH) depends upon the degree of nitration, the degree of the modification of the cellulose and the camphor content of the solvent. The max. soly. of a nitrate prepd. from a bleached cotton wool of Cu no. 1.02 (degradation of the cellulose prevented as far as possible) is obtained when the N content is about 11%; this is sol. in 8% EtOH-camphor. Nitrates with higher or lower N contents require a higher camphor content; the N limits appear to be 9.87 to 12.30%, and other nitrates do not completely dissolve in EtOH of any camphor content. The soly. which qualifies a nitrate as the material for celluloid is conveniently expressed by the least % amt. of camphor in an EtOH-camphor soln. in which the nitrate is completely sol. This is termed the "camphor no." Standard nitrate must have a camphor no. between 8 and 10. The viscosity of the nitrate in EtOH-camphor is influenced by the same factors as the soly. With the increase of camphor in the solvent, the viscosity decreases at first, reaches a min., and then rises. The min. value varies with the nature of the nitrate but generally is the point where the camphor content of the solvent is 35%. The min. viscosity is obtained when the H_2O content of the solvent is 3.5%; the nitrate ppts. when the H_2O content is about 10%. The viscosity is also varied by replacing EtOH

partially or totally by some other solvent, such as AcMe. The soly. and viscosity of the nitrate have no direct relation to the stability of the nitrate but they have an intimate influence on the stability of the resulting celluloid. Celluloid made from a nitrate with camphor no. 8-10 and of max. viscosity is of high stability. The more homogeneous the structure of the celluloid, the higher is its stability. C. J. WEST

Cellulose acetate. ABEL CAHLE. *Bull. soc. ind. Rouen* 48, 431-4(1920).—Polemic (cf. Deschiens, *C. A.* 14, 2705). A. PAPINEAU-COUTURE

Paper research literature. VII (revised). List of contributions by members of the Bureau of Standards, Dept. of Commerce, 1910-1922. F. A. CURTIS AND C. J. WEST. *Paper Trade J.* 76, No. 6, 47-52(1923).—An annotated bibliography of 45 titles. C. J. WEST

Determination of the effect of pressure on the strength of test sheets in the strength-testing of pulp. E. P. CAMERON. *Pulp Paper Mag. Can.* 21, 127-34(1923).—The strength developed is independent of the length of time the pressure is applied (within the limits of the speed of the machine used, a 60,000-lb. Riehle testing machine). The strength increases with increase of pressure applied, other conditions being const. This increase is more marked at the lower pressures used and on the lighter basis-wt. sheets. The strength varies inversely with the basis-wt., other conditions being const. It varies independently of the moisture content before pressing. For the moisture contents used, 75% was found to be the optimum. It seems imperative that the basis-wt. of the test sheets and the pressure applied in their formation should be accurately specified in any standard method of testing pulp for strength. C. J. WEST

Coloring of paper. L. MANN. *Dyestuffs* 23, 933-40(1922); 24, 4-9(1923).—A short discussion of the color-room is followed by some interesting material on the selection of the proper dyes for a required shade of paper, including discussion of fastness requirements, raw materials and their effect on permanency, 2-sidedness, etc. The 2nd part gives a list of colors for various grades of papers. C. J. WEST

Chemical composition of various German commercial sulfate pulps. CARL G. SCHWALBE. *Zellstoff u. Papier* 2, 279-84(1922).—Analytical values for 15 pulps are given. Cf. values reported for Swedish pulps by Sieber, *C. A.* 17, 633. C. J. WEST

Properties of wood in paper making. BJARNE JOHNSEN AND H. N. LEE. *Pulp Paper Mag. Can.* 21, 111-4; *Paper Trade J.* 76, No. 5, 53-56; *Paper Mill* 47, No. 4, 10, 12, 46(1923).—The effect of phys. and chem. properties of the wood on economy and quality, particularly in the sulfite process, is discussed. Among such properties are: density and rate of growth, cellulose content, degree of soundness of the pulp wood; in the manufg. process, the density of the wood, moisture content of chips, time of seasoning and rate of penetration of cooking liquor are important. C. J. WEST

Reddening of sulfite pulp. H. E. WALBERG. *Svensk Pappers-Tid.* 1922, No. 22, 401-2; *Paper Trade J.* 76, No. 6, 53(1923).—The reddening of sulfite pulp is caused by the oxidation of impurities in the pulp, such as ferrous salts and org. substances, which give red ferric compds. The reaction takes place especially in a moist atm. or in the presence of oxidizing agents, such as bleach liquor, and is accelerated by small quantities of Cu salts in the pulp. The color can be avoided by the use of a cooking acid as free as possible from Fe salts. The red color can be removed by washing the pulp with very dil. H_2SO_3 . C. J. WEST

How far can the pulp-mill go in utilizing decayed insect-killed or other inferior wood in the manufacture of pulp? J. S. BATES. *Pulp Paper Mag. Can.* 21, 77-80(1923).—General survey of the field of the use of inferior pulp wood. In ground-wood processes decayed wood gives a medium to high yield but the quality of the product is poor. Long storage of infected ground wood should be avoided. The sulfite process gives a comparatively high yield and the quality is fairly good. This process is suitable

for producing low and medium grades including newsprint sulfite. The soda process gives a rather low yield and only fair quality. The kraft process gives a medium yield and the quality is fairly good. This method of utilization has a wider application than any of the others and the results with decayed wood may be considered favorable when the proportion is not too high. The handling of inferior wood from the forest until it is made into paper is an important problem and requires careful investigation. C. J. W.

Presence of acetal in sulfite spirits. AAGE W. OWE. *Papierfabr.* 20, 1564-5 (1922).—Examn. of the 1st runnings of sulfite spirits, b. 101-2°, showed it to be practically pure acetal. This is important analytically because its presence will influence the detn. of AcH. The amt. of acetal may be detd. from the difference in the AcH content before and after hydrolysis with HCl. C. J. WEST

Some observations on sulfite digesting. B. THORBJORNSEN. *Svensk Pappers Tidning* 25, 196-9, 252-4, 307-10 (1922).—A descriptive résumé of the Swedish pulp industry, with many data indicating the most economical working of the various steps. Detns. on 18 samples of wood of sp. gr. 0.44-0.57 gave water content 14.1-38.4%, wt. in kg. per m.³ of dry wood 368-457 (av. 415), cellulose content 52.2-60.1% (av. 57.0) and cellulose content in kg. per m.³ 204-260 (av. 237). The cellulose content of spruce is nearly proportional to the wt. per vol. of dry wood. A digester will hold 2.2% more chips with 40% moisture than with 20% moisture; 1 kg. absolutely dry wood gives 0.47-0.48 kg. pulp. Each m.³ of digester capacity should yield 73.9 kg. bleached pulp and 78.1 kg. raw pulp. From the air driven out of the chips during digesting the sp. gr. can be detd. by $\text{vol. of wood (wt./sp. gr.)} + \text{vol. of digesting water} + \text{vol. acid pumped in} = \text{capacity of digester} - \text{vol. of air}$. Air from 1 m.³ of wood with 20% moisture = 582 l. Treatment of chips with steam to remove the air before addn. of acid is described. Chips not thus steam-treated require 12.1% less acid and the acid does not penetrate the wood completely. Wood treated with alkali before addn. of acid turns dark; precautions necessary in such cases are given. Tables show the proper amt. of acid to use in indirect digesting of wood with 20, 30 and 40% moisture on the basis that 2.50% free S and 1.00% combined S give best pulp. For direct digesting dry wood absorbs acid to 15% of its vol. For different moisture contents the proportion of free S and of combined S in the acid must be changed (tables given). The calcn. of the amts. of steam and of acid necessary for the digester is illustrated. One ton of raw sulfite cellulose uses chemically an amt. of heat corresponding to 100 kg. of steam. A detailed table of heat needed for the different parts during indirect digesting shows that wood with 20, 30 and 40% moisture uses 1911 kg., 1931 kg. and 1970 kg. steam, resp., per ton of pulp. The amt. of heat needed in upright and in rotary digesters during direct digesting is about the same as for indirect; the moisture content has less effect in the upright digesters. A rotary digester and 3 types of upright digesters used in Sweden are diagrammed and their operation is described. Some of the products of digesting are easily sol. in water, some are sol. in acid soln., but the lignin dissolves with difficulty. Mathematical formulas show the effect of different factors on the dissolving of lignin; the results agree well with observed facts. All disintegration of the fibers is caused by the free acid and the disintegration is proportional to the amt. of lignin dissolved by the free acid. Absence of bisulfite gives woody, brittle and dark-colored pulp. A graph illustrates this and conditions governing the kind of pulp obtained are discussed. Graphs for direct and for indirect digesting are given and compared; the quality of the pulp obtained by the 2 methods is not markedly different, but the temp. and pressure must be carefully regulated. W. SEGERBLOM

Value of waste lime from cellulose factories as soil amendment (VON FEILTZEN)

15. Dyeing cellulose acetate (Brit. pat. 187,964 and U. S. pats. 1,442,631 and 1,440,501)

25. Tanning material from cellulose waste sulfite liquor (U. S. 1,441,243) 29. Evaporating liquids generating acid vapors (U. S. pat. 1,440,026) 13.

Cellulose ethers. H. DREYFUS. Brit. 187,639, April 19, 1921. Relates to the manuf. of cellulose ethers as described in 164,374 (C. A. 16, 493), 164,375 (C. A. 16, 493), and 164,377 (C. A. 16, 494). According to the present invention the quantity of H_2O present during the etherification is reduced by the addn. of agents capable of binding H_2O by chem. combination, to the proportion specified in the prior specifications (C. A. 16, 493); the amt. of caustic alkali or other base used in the etherification is at least equal to and preferably exceeds in the ratio of 3:1 to 19:1 or more the wt. of H_2O present or added. By the use of such water-binding agents, the alkali is more firmly seated on or united to the cellulose, and the etherification may be carried out with reduced quantities, even down to theoretical quantities, of alkali and etherifying agent. Suitable water-binding agents are the oxides of the alkali and alk. earth metals, the hydrides of Ca and Mg, the metals, Ca, Ba, and Na, and sodamide and Na ethylate powder. The compds. formed by the union of the water-binding agent with the water present may constitute in part or wholly the alkali or base necessary for the etherification; the hydroxides of the alk. earth metals may be employed as the base but with these, being weaker, the etherification may be conducted at temps. higher than those necessary with the caustic alkalis. In order better to control the temp. during the removal of the H_2O , the water-binding agents are preferably incorporated in the presence of diluents or solvents such as C_4H_{10} , C_2H_6 , CCl_4 , ether, or ligroin, and the mixt. is strongly cooled; the solvents or diluents may also be employed during the etherification. The initial material is either cellulose or a near conversion product insol. in dil. alkali at ordinary temps., or alkali-sol. cellulose derivs. from which such alkali-insol. cellulose or conversion products may be reconstituted, or such reconstituted products themselves. Examples are given. Cf. 12,854, 1912 (C. A. 7, 3839) and 6035, 1913 (C. A. 8, 2947).

Cellulose ethers. L. LILIENFELD. U. S. 1,441,989, Jan. 9. Cellulosic material is impregnated with a soln. of caustic alkali and is then immediately treated with an etherifying reagent without "ripening" or removal of excess alkali.

Cellulose ether composition. S. E. SHEPPARD. U. S. 1,441,181, Jan. 2. A compn. adapted for making *films, varnish or molded articles* is formed of cellulose ethyl ether 100–200 and tetrahydronaphthalene 15–30 parts, with solvents and modifying reagents.

Cellulose acetate. W. J. STEVENSON. U. S. 1,441,541, Jan. 9. Bleached sulfite paper pulp is acetylated with glacial HOAc, Ac_2O and $ZnCl_2$ to obtain cellulose acetate which is more stable and more readily dyed than cellulose acetate from cotton.

Cellulose acetate composition. H. DREYFUS. U. S. 1,440,006, Dec. 26. A compn. adapted for *films, varnishes or artificial silk* is formed of cellulose acetate 100 and cyclobutanone 1000 parts or a mixt. of cyclobutanone with MeOAc, acetone or alc., with or without triphenyl phosphate.

Hydra-oxy-cellulose; viscose; artificial silk; plastic compositions; substitutes for horn, amber, ebonite, rubber, wood, leather, etc.; sizes; abrasive and polishing materials. C. C. L. G. BUDDE. Brit. 184,610, May 28, 1921. A cellulose product adapted for the manuf. of viscose, and termed hydra-oxy-cellulose is prepd. by treating cellulose admixed with H_2O first with gaseous Cl in excess of the amt. required to sat. the H_2O present, and afterwards with strong HCl, preferably the acid produced in the first stage of the process. For wood pulp the proportions are cellulose 100 parts, H_2O 100 parts, Cl 10 parts; in other cases a larger proportion of Cl may be necessary. In any case the proportion of H_2O lies between $1/3$ and twice the wt. of the cellulose material. By the usual xanthogenation process, the cellulose conversion product is converted into a viscose which at the usual concns. has the character of a jelly. The product is used in the manuf. of the various articles mentioned in the title.

Viscose; artificial silk; films. NAAMLoozE VENNootschAP HOLLANDSCHE KUNST-ZIJDE INDUSTRIE. Brit. 183,476, July 20, 1922. In the manuf. of artificial silk, films, etc. from viscose, an aq. ext. of the parts of the plants is added either to the pptg. bath contg. H_2SO_4 and sulfates, or to the viscose itself. Salts of NH_3 , NEt , pyridine, etc. may also be added to the bath. The H_2O exts. are obtained by boiling the material with H_2O under pressure, acidifying the ext. heating preferably to the b. p. filtering, and if necessary, concg., preferably *in vacuo*; the salts for the pptg. bath may be added to H_2O during the extn. process, or they may be added to the ext. A similar procedure is adopted in the case of acid alk. extns.; a suitable acid extracting medium is 5% H_2SO_4 , and as an alk. extracting medium, solns. of NaOH , soda, or NH_4OH may be employed. The exts. may be treated with bleaching agents either during or preferably after the extn.

Recovering values from carbonaceous wastes. J. E. PLUMSTEAD. U. S. 1,442,494, Jan. 16. Soda pulp mill waste liquor is heated to effect evapn. and incineration and the gaseous products from the heating are afterward brought into contact with the insol. material which remains from extn. of the residue in order to obtain a *fuel* for heating the incinerating evaporator.

Recovering pulp from waste paper. S. KUMAGAE and T. CHIBA. Brit. 187,805, Sept. 26, 1921. Waste printed paper is boiled in a soln. contg. soap, $\text{Na}_2\text{S}_2\text{O}_4$, and a waste fluid known as "tofu whey," which remains after prepg. a food of Japan and China known as "tofu" from the soy bean. The printing ink is thus loosened, and is removed by heating and washing.

Treating paper for spinning, etc. E. FUES. Brit. 187,987, Oct. 28, 1922. Parchment paper is rendered suitable for spinning into threads, etc., by treating it with solns. of $\text{Al}_2(\text{SO}_4)_3$ and HCHO and then drying it quickly on rolls at 100° ; the treated paper is prevented from subsequently becoming brittle by drying it at a lower temp., *e. g.*, $60\text{--}85^\circ$, for a longer period, and then for a short period at a higher temp. The quantity of acid substances used may also be reduced, *e. g.*, to less than 1% of $\text{Al}_2(\text{SO}_4)_3$ by wt. of dry paper, in which case the paper can be dried quickly at 100° without subsequent cracking. The % of HCHO used may be increased, and substances such as benzoic and salicylic acids may be added to give a disinfectant action.

Paper machine. P. E. DUDLEY and H. BOICE. U. S. 1,441,332, Jan. 9. An apron of textile fabric impregnated with a pyroxylin compn. carries the flow from the flow box to the Fourdrinier screen.

24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

Bibliography [on explosives]. T. L. DAVIS. *Mem. poudres* 19, 200–15(1922).—A list of books, pamphlets, journal articles and patents published during 1918–20.

C. G. STORM

The dehydration of nitrocellulose by displacement. PONCHON. *Mem. poudres* 19, 81–145(1922).—A detailed account of a plant study of the proper conditions for economical and efficient dehydration of nitrocellulose in the manuf. of *smokeless powder*, including investigation of such factors as quantity and strength of EtOH used, rate of displacement, max. pressure, % H_2O in nitrocellulose, etc. The best results were obtained by using 22 kg. EtOH (93%) for 20 kg. of nitrocellulose, and operating by a definite procedure. The quantity of recovered EtOH requiring rectification was greatly reduced by fortifying a portion of the recovered EtOH with fresh 95% EtOH .

C. G. STORM

The toxicity of the fumes from chlorate explosives. H. KAST and A. HAID. *Z. f. Schiess-Sprengstoffw.* 17, 145–9(1922).—Gaseous products of detonation of 8 varieties

of chlorate blasting explosives contg. 65–90% NaClO_3 or KClO_3 with varying proportions of nitro compds. and carbonaceous materials were obtained by exploding 20-g. samples in a Trauzl Pb block in a 100-l. steel chamber. Concn. of CO from 1% to 3% were found. When the explosives were burned instead of detonated, less than 1% CO was found, while NO_2 was produced in amts. usually from 0.1% to 0.2%. The evolution of CO from mixts. contg. more than enough O for complete oxidation was not confined to chlorate explosives. *Donarite*, contg. NH_4NO_3 , 80, TNT 12, nitroglycerin 4 and wood meal 4%, gave a similar result. The toxicity of CO and NO_2 is discussed. The effects of these gases are increased by the presence of alkali chloride dust and soot in the atm. Many of the chlorate explosives readily develop a tendency to become insensitive and to burn instead of detonating. C. G. SORM

Explosives from the air. T. I. DAVIS. *Army Ordnance* 3, 193–5(1923).—A review of the method of production of liquid O and of N compds. from the air for the manuf. of a wide variety of explosives. Porous Al cylinders may be used in place of C as the absorbent cartridge for liquid O explosives. *Nitroguanidine*, produced from CaCN_2 , explodes with no visible flash and a cool flame. It renders nitrocellulose powder coated with it, flashless. While the temp. of the explosion products of military smokeless B. F. is 2676° , black sporting powder 3530° , gelatin dynamite 3545° , 75% dynamite 3161° and nitromannitol 3429° , that of nitroguanidine is 907° . *Nitrosoguanidine* is a "primary explosive" in that it explodes from fire or shock but it is lacking in brisance, and, though it produces much gas, this gas is cool. "A small heap of the material, placed in the open palm of the hand, may be exploded by a match, but the explosion produces no visible flash or perceptible sensation of shock or of heat." C. J. M.

The decomposition of mercury fulminate. A. LANGHANS. *Z. ges. Schiess-Sprengstoffw.* 17, 122–6, 131–3, 150–3, 159–62(1922).—The insensitive product resulting on long heating of $\text{Hg}(\text{ONC})_2$ (cf. C. A. 16, 2603) was further investigated. The Hg contg. of both gray and white $\text{Hg}(\text{ONC})_2$ increased from 70.42% to 76.4% in 72 hrs. heating at 82° and the resulting products were insensitive to flame. The increase in Hg content is proportional to the time of heating. Mixts. of $\text{Hg}(\text{ONC})_2$ and KClO_3 became insensitive after 144 hrs. at 80° . The brown decompn. product has the same cryst. form as $\text{Hg}(\text{ONC})_2$. It is apparently a mixt. of Hg^+ and Hg^{++} compds. *Blasting caps* stored 2 yrs. at 55° no longer detonated normally. The fulminate was colored strongly yellow and contained 43% of noncombustible material insol. in H_2O , EtOH, pyridine, and $\text{Na}_2\text{S}_2\text{O}_3$. With $\text{Hg}(\text{ONC})_2$, HNO_3 produces soln. with decompn., the rate of decompn. depending on concn. of HNO_3 . Fuming HNO_3 and aqua regia cause violent evolution of NO_2 and other gases, the soln. contg. various Hg compds. A drop of concd. H_2SO_4 on $\text{Hg}(\text{ONC})_2$ causes detonation, but if the fulminate is added to the acid in small amts. at a time there is no explosion but rapid decompn. with sepn. of C. The soln. contains oxalic acid. Cold Na_2SO_3 (25% soln.) converts fulminate in 24 hrs. into a new white cryst. compd.; heating causes evolution of NH_3 . Both $\text{Na}_2\text{SO}_3 \cdot \text{HgSO}_3(+\text{H}_2\text{O})$ and $\text{Na}_2\text{SO}_3 \cdot 2\text{HgSO}_3(+\text{H}_2\text{O})$ were identified in the product. NaHSO_3 gives a black ppt. of Hg + HgS. Solns. of $\text{Hg}(\text{ONC})_2$ in $\text{Na}_2\text{S}_2\text{O}_3$ deposit HgS on standing. As bearing on the $\text{Na}_2\text{S}_2\text{O}_3$ method for *detr.* of $\text{Hg}(\text{ONC})_2$, L. found that the alkalinity of a soln. of 0.3 g. $\text{Hg}(\text{ONC})_2$ in $\text{Na}_2\text{S}_2\text{O}_3$ soln. decreased on standing at a rate inversely proportional to the concn. of the $\text{Na}_2\text{S}_2\text{O}_3$ soln. Dissolved in 2.48% $\text{Na}_2\text{S}_2\text{O}_3$ soln., 0.3 g. $\text{Hg}(\text{ONC})_2$ required 42.00 cc. N H_2SO_4 soln. for neutralization after 2.5 min., and only 0.88 cc. after 36 hrs. When 20% $\text{Na}_2\text{S}_2\text{O}_3$ soln. was used the vol. of H_2SO_4 required was 42.03 cc. after 2.5 min. and 16.74 cc. after 36 hrs. The formation of H_2SO_3 by reaction of the fulminate with the $\text{Na}_2\text{S}_2\text{O}_3$ on standing was proved by a test with BaCl_2 , and is probably accelerated in dil. solns. by the action of H_2O . The wt. of BaSO_4 produced after standing 15 min. increased with the wt. of $\text{Hg}(\text{ONC})_2$ dissolved

in a given vol. of $\text{Na}_2\text{S}_2\text{O}_3$ soln. and decreased as the vol. of the $\text{Na}_2\text{S}_2\text{O}_3$ soln. used for a given wt. of $\text{Hg}(\text{ONC})_2$ was increased. *Electrolysis* of 3-4 g. of fulminate in 150 cc. of 5% KBr soln. gave practically the theoretical amt. of Hg. Similar results were obtained by using as electrolytes dil. solns. of $(\text{NH}_4)_2\text{C}_2\text{O}_8$, NaOCl, NaOBr, NaOI, Na_2S , and NaCl. Erratic results were obtained with solns. of KCN, NH_4OH and HNO_3 , and negative results with NH_4CNS , KI and $\text{Na}_2\text{S}_2\text{O}_3$ solns. C. G. STORM

Additions, removals and changes in Permissible List of Explosives from March 15 to Dec. 31, 1922. S. P. HOWELL. Bur. of Mines, *Repts. Investigations* No. 2430, Jan. 1923. Mimeographed. 4 pp. CHARLES E. MUNROE

Novelties in initial priming substances. LOTHAR WÖHLER. *Z. angew. Chem.* **35**, 545-9(1922).—A detailed historical account of initial priming substances from the discovery of $\text{Hg}(\text{ONC})_2$, and its application by Nobel to detonate dynamite down to cyanuric triazide, with a rehearsal of the characteristics of a very large number of the substances that have been found to serve this purpose, many of which are but little known. CHARLES E. MUNROE

Effect of cartridge diameter on the strength and sensitiveness of certain high explosives. SPENCER P. HOWELL AND J. E. CRAWSHAW. Bureau Mines, *Repts. Investigations* No. 2436, 9 pp.(1922).—From results of tests of 40 and 60% L. F. gelatin dynamites and of 40% L. F. ammonia dynamite, in cartridges of $7/8$, $1\frac{1}{4}$ and $1\frac{1}{2}$ in. diam., it was found that both the rate of detonation and sensitiveness to explosion by influence increase with increase in diam of cartridge; also that gelatin dynamites rapidly decrease in sensitiveness to detonation and explosion by influence on ageing while the ammonia dynamite was very little affected; the insensitiveness of gelatin dynamites to detonation and explosion by influence on ageing proceeds more rapidly the smaller the diam. of cartridge and with 60% strength L. F. gelatin dynamite than with 40% strength L. F. gelatin dynamite. The effect of cartridge diam. is very important from the standpoint of safety in use as the more rapid decrease in sensitiveness to detonation of the smaller diam. is likely to cause more misfires, while the decrease in sensitiveness to explosion by influence is likely to cause more partial failures from foreign material in the borehole. Further, insensitive gelatin dynamite sometimes burns in the borehole instead of detonating, and, on burning, gives off large quantities of oxides of nitrogen which are very poisonous, even in small percentages. Also, in the smaller diams. of cartridge the proportion of paper wrapper to explosive ingredient is greater, and as most explosives on detonation give greater or less quantities of noxious gases (chiefly CO), the smaller diams. of cartridge will give the greater quantities of poisonous gases, because of this increased ratio of paper wrapper. Investigation of the samples which failed to detonate shows the great importance of well tamping gelatin dynamite shots, as this confinement will insure better and more complete detonation. Both economy and safety in the use of explosives are decreased by the use of cartridges $7/8$ in. in diam.; drill holes should accommodate cartridges of not less than $1\frac{1}{4}$ in. diam. C. E. M.

Conceptions regarding the explosion of various organic dusts. P. BEYERSDORFER. *Ber.* **55B**, 2568-96(1922).—An account of an investigation of the conditions necessary for the explosion of sugar dust, as an example applicable to all other org. dusts. The factors influencing dust explosions may be either thermal or elec. The ignition temp. of sugar dust in air was $410^\circ (\pm 1^\circ)$, in O_2 371° . Small quantities of ozone lowered the former value about 3° and the latter 4° . The ignition temp. depends upon the O_2 content of the gases and the thermal cond. of the inert gases accompanying the O_2 . This is shown graphically. CO_2 causes more extinguishment in this case than N_2 . In a thermal sugar dust explosion there is a preliminary gasification of the sugar (like coal) and then ignition of these "sugar gases." The upper explosive limit is given as 13.5 g. dust per cu. m. air and the lower limit as 17.5 g. per cu. m. air. B.'s theory of

elec. sugar dust explosions, as in an a. c. field, is the preliminary formation of O_2 and N_2O_4 , which subsequently react with the sugar dust and explode. By fanning in air sugar dust may acquire a charge of more than 10,000 v. The term "aerosol" is suggested for dust-air mixts. The application of an isoelec. point in a sugar "aerosol" will cause explosion. O_2 adsorption may be a factor in causing explosion, but terrestrial magnetism is not, neither is triboluminescence. The article is accompanied by drawings and description of the app. used, as well as curves and numerous tables. I. J. T.

The explosibility of methane-air and gasoline-air mixtures as related to the design of explosion-proof electric motors. E. J. GLEIM. Bur. Mines, *Repts. Investigations* No. 2422, 7 pp.(1922).—A motor, which is to be used in a place where explosive mixts. of highly volatile gasoline vapors and air may accumulate, should have twice the protection against communicating an explosion within it to the outside atm. that it would require in order to be used safely in explosive atms. of CH_4 and air. For less volatile gasolines the degree of protection required might perhaps be somewhat less, although it should be remembered that the heavier constituents of such a gasoline will not long remain vaporized unless heated; hence the more volatile constituents will still be the ones to be guarded against. On account of the greater pressures resulting from explosions of the gasoline-air mixt. than from CH_4 mixts., the casing of a motor for use in the former mixts. would need to be mechanically stronger by about 45% to withstand the internal explosion pressures. For less volatile gasolines it might be expected that the pressures would not reach such high values; consequently the mech. strength of the motor casing might be reduced below that for the more volatile gasolines. In protecting a motor for use where there may be explosive gasoline-air mixts., there may also be condensed vapors on the surface near the motor or even in the motor and constituting a fire hazard (should there be an explosion) which should be taken into consideration. In other words, when a CH_4 -air mixt. explodes there is no "residual" or condensation to give flame other than that of the burning gas, unless some different combustible such as coal dust is present, while in the gasoline-air explosion, any condensed gasoline vapors or liquid gasoline close at hand would catch fire and so add to the damage caused by the explosion. If gauzes were used as a means of protecting the motor it is to be expected that condensation and the less volatile matter adhering to them would serve to hold dust and dirt in the meshes and thus weaken and possibly destroy the effectiveness of the gauzes. The lower ignition temps., the higher rate of propagation, and the higher calorific value of gasoline, together with the fact that the explosive limits are much lower than those of CH_4 -air mixts., point at once to greater difficulties in designing a motor for use in gasoline-air mixts. than for CH_4 -air mixts. It is believed that the most suitable design would be a totally inclosed type of motor having flanges at least one in. in breadth and a casing sufficiently strong to withstand any internal explosions of gasoline-air mixts., without rupture or discharge of flame. C. E. M.

The pressures developed in gaseous explosions. W. T. DAVID. *Engineering* 114, 791-2(1922).—There is here shown a record of pressure curves, made with an optical indicator provided with a high-frequency spring, which exhibits no trace of the indicator oscillations common to the records heretofore taken with the pencil indicator, and which is believed to show the development of pressure with a high degree of accuracy. With a mixt. of coal gas + air, ignited by an elec. spark placed in the center of the vessel, the pressure rises slowly at first, then rapidly until a max. rate is attained which remains const. for a time, when it begins to decrease slowly owing to the cooling action of the walls of the contg. vessel. The period elapsing between the moment at which the pressure begins to rise and that at which it attains its max. value is the "time of explosion." The greater part of the burning takes place during the explosion period yet a not inconsiderable proportion remains unburnt at the moment of max. pressure and this

is burnt as the mixt. cools. An appreciable vol. of inflammation also appears in the "pre-pressure period," which is that period elapsing between the moment of the passage of the ignition spark and that when the pressure begins to rise. It has been observed that flame completely filled the explosion vessel some little time before the attainment of the max. pressure. During the explosion of a 10% mixt. of coal gas + air at atm. density, in a vessel of 6.2 cu. ft. with 0.25 secs. time of explosion, Hopkinson found the flame completely filled the vessel approx. $\frac{1}{10}$ sec. before the max. pressure of 82 lbs. per sq. in. was attained, the pressure at the moment being 70 lbs. per sq. in. The portions of gas first ignited undergo adiabatic compression due to later inflammation of the surrounding portions and temp. distribution at the time of max. pressure is therefore far from uniform; H. found a temp. of 1900° for the hot core of the flame and 1600° for the mean temp. of the flame. D. describes in detail the method of expt. and, with graphs, discusses at length the effect of position of spark on pressures developed, mixt. strength, density, nature of the interior surface of the explosion vessel, and the effect of inert CO_2 upon explosion pressures. An interesting observation is that, with a 15% coal gas + air mixt., the max. pressure was about 3% greater, and the rate of cooling much slower, in a polished vessel than in the same vessel when the walls were blackened.

CHARLES E. MUNROE

Experiences in unique explosions. H. STAUDINGER. *Z. angew. Chem.* 35, 657-9 (1922).—An account of explosions in various industries classified by causes. An explosion was caused in Zurich in 1919 during the manuf. of acetoacetic ester from Ac_2O and EtOH by the violent catalytic activity of NaHSO_4 accidentally left in the reaction vessel. Several examples are cited of explosions due to the production of endothermic compds., e. g., phenyl azide and azodicarbonic ester. Explosions from nitro compds., particularly one occurring in 1920 during the distn. of *o*- and *p*-nitrotoluenes, are mentioned, also explosions in the presence of oxygen under high pressure, as in the autoxidation of α,α -diphenylethylene, and by alkali metals as in the violent explosion following the treatment of oxalyl chloride or bromide with Na-K alloy. A wide range of examples is given.

CHARLES E. MUNROE

Efficiency of the Palmer apparatus for explosive carbonaceous dusts. L. J. TROSTEL. *J. Am. Soc. Heating & Ventilating Engrs.* 28, 853-8 (1922).—In its study of combustible dusts occurring in various industries the Dust Explosion Lab. of the Bur. of Chemistry has investigated the efficiency of the Palmer dust sampler (*C. A.* 11, 1228; 14, 3388) devised for use in hygienic studies, for measuring such heavy suspensions of dust as occur in grain elevators, cereal mills, food factories and chem. works. The app. was tested on 10 dusts, of markedly different chem. and phys. properties, on a wt. basis. The sampler retained, on an av., 98.2% of the dust added to it; its efficiency appeared not to be affected through varying the rate of sampling from 3 to 5 cu. ft. per min., while it appeared to increase with the wt. of dust collected up to certain limits; the max. wt. possible to collect efficiently ranges from approx. 1.5-3 g. depending on the nature of the dust; the efficiency is higher as dusts of large-sized particles are being collected.

CHARLES E. MUNROE

Explosion involving 12-bore sporting cartridges at Guilford, Bury St. Edmunds. A. COOPER-KRY. *Special Rept. H. M. Insp. Exp.* 241, 5 pp. (1922).—A "loader" at a "shooting" was killed by the explosion of shot gun cartridges carried in his coat pocket. The fact that, though some 200,000,000 such cartridges are used annually in England, no such accident has heretofore been known, and the peculiar appearances of the remains of cartridges found in the pocket of this man's coat combined to indicate that by some chance he had also a detonator in his pocket. Experiments showed that the unusual conditions found could be reproduced by the explosion of a detonator among shotgun cartridges situated as these were.

CHARLES E. MUNROE

Curious causes of gasoline fires and gas explosions. A. H. GILL. *Ind. Eng. Chem.* 15, 140(1923).—The various accidental explosions reviewed appear to have been initiated by accumulated static elec. charges. CHARLES E. MUNROE

Explosions in liquid air rectification plant. ERNEST FYLEMAN. *J. Soc. Chem. Ind.* 42, 37-9T(1923).—Violent explosions in the baths of liquefied O and air in rectifying columns have been so frequent that to reduce the danger and damage it is now customary to install the columns in deep pits. There has been an impression in the industry that these explosions were due to the presence of C_2H_2 and in expts. where mixts. of solid C_2H_2 , liquid O and oil were stirred in Cu vessels very violent explosions ensued. While it is apparent that in works where CaC_2 and C_2H_2 are stored or used C_2H_2 might gain access to the air intake of the compressor it is difficult to account for it in liquefied gas in plants located in the open country where the atms. is presumably uncontaminated. P. found that in a rapid current of air compressed under 30 atms. C_2H_2 was produced from "compressor" oil or paraffin wax at 350° , and from olive oil at 320° . Exactly what initiates the explosion is yet unknown. It is surmised $CH:C:C:CH$, which was obtained as a yellow Ag salt, or a static charge due to the outrush of the air or O, contg. particles of solid C_2H_2 , when a valve was opened, may be the initiator. Keeping the valves and other parts of the compressors cool, employing a suitable oil of high flash point and banning carbide in any form from the neighborhood of the plant has proved a sufficient safeguard but F. suggests also passing the air through tubes loaded with $1/8$ in. particles of a compn. made by hydrating 6 lbs. of plaster of Paris with a soln. of 200 g. of $KMnO_4$ and 20 g. Na_2CO_3 in 2 l. of H_2O to which 100 cc. of a 10% soln. of $AgNO_3$ has been added for this will remove the C_2H_2 . CHARLES E. MUNROE

Toxicity of aromatic nitro compounds (STUKOWSKI) 11H.

Explosives. E. VON HERZ. Brit. 187,012, July 11, 1921. Mixts. of Pb azide and Pb trinitroresorcinate for use as explosive priming compns. are prepd. by the simultaneous pptn. of the two salts or by the pptn. of one salt from a soln. contg. the other salt in suspension. E. g., Pb azide is pptd. by the addn. of Na azide to a soln. of Pb acetate contg. Pb trinitroresorcinate in suspension.

Explosives. H. RATHSBURG. Brit. 185,555, June 27, 1921. Explosive salts of tetrazole or triazole or their derivs. are used in detonators, percussion caps, etc. These salts may be mixed or pptd. simultaneously to form double or mixed crystals with other ingredients such as HN_3 , nitrophenols and their substitution products, also 1,3,4,5-(O_2N) $_2C_6H_2(NO)_2$ and (O_2N) $_3(ON)C_{10}H_2OH$. The salts may also be granulated with paraffin or resins dissolved in benzene, xylene, or CCl_4 . Blasting detonators may contain a top charge of such compns., e. g., a charge of Pb azotetrazole over Pb or Cd tetrazyl nitride over tetranitromethylaniline. The prepn. of the following substances is described: (1) tetrazole, from dil. HN_3 and HCN, or by reduction of diazotetrazole salts by $SnCl_2$, Sn or alc., or by oxidation of naphthyltetrazole or aminophenyltetrazole with $KMnO_4$; (2) tetrazylazoisimide, by splitting tetrazenes or treating tetrazylhydrazine with $NaNO_2$ and HCl; (3) azotetrazole, by oxidizing aminotetrazole in alc. solns. with permanganates or persulfates, the aminotetrazole being obtained synthetically from H_2CN_2 and HN_3 or in the presence of $AcONa$ from guanylazide salts formed when aminoguanidine salts are diazotized; (4) oxyazotetrazole, by treating diazotetrazole salts with CO_2 ; (5) diazoaminotetrazole, by diazotizing aminoguanidine salts with NaN_3 in $HOAc$ soln.; (6) diazotetrazole, by diazotizing aminotetrazole; (7) bistetrazole, from $(CN)_2$ and HCN soln.; (8) phenyltetrazolecarboxylic acid, by boiling phenyltetrazole cyanide with alc. KOH; (9) methylmercaptotetrazole, by diazotizing methylthiosemicarbazide; (10) phenylethylenedioxytetrazole, by decomp. with alc. KOH

the phenylacetamide salt obtained during the diazotizing of phenylacetamide nitrate; (11) β -naphthyldioxytetrazole, by decomposing the β -naphthenylamide salt obtained in diazotizing β -naphthenylamide; (12) phenylglycolenyldioxytetrazole, by decompn. of phenylglycolenylamide salts obtained by diazotizing phenylglycolenylamide; (13) benzenyldioxytetrazole, by diazotizing acid benzenylamide and decomposing the benzenylamide salt thus obtained; (14) *m*-nitrobenzenyldioxytetrazole, by diazotizing *m*-nitrobenzenylamide; and (15) *p*-tolenyldioxytetrazole, by diazotizing *p*-tolenylamide and decomposing the resulting *p*-tolenylamide salt with alc. potash lye.

Preventing explosions in mines. H. KRUSKOPF. Brit. 186,763, Aug. 6, 1921. Addn. to 161,474. An explosion-arresting powder for use in mines in the manner described in the principal patent consists of natural loamy earths, such as ooze, loam, clay, etc., without admixts. of other substances, dried at moderate heat and crushed to a fine dust.

Perchlorate explosive. R. M. COOK. U. S. 1,440,767, Jan. 2. Explosives are formed of NH_4ClO_4 21-30, MnO_2 4-7, NaNO_3 17-47.5, TNT 23-26, nitroglycerin, tetranitrodiglycerin or dinitromonochlorohydrin 2% and small amts. of CaCO_3 , S or wood meal. U. S. 1,440,768 specifies similar explosives in which KClO_4 is used instead of NH_4ClO_4 .

Blasting cartridge containing liquid air. G. WEBER. U. S. 1,441,957, Jan. 9. A blasting cartridge is formed of liquid air packed in a rigid watertight cardboard casing together with C_{10}H_8 or paraffin with or without powd. Al, Si, Sb, Mg, Fe, Fe oxide or silicides. Cf. C. A. 16, 1321.

Blasting charge containing liquid air. G. WEBER. U. S. 1,440,041, Dec. 26. Liquid air is used with C_6H_6 , petroleum, C_{10}H_8 or other org. combustible material and with Fe ore dust, Al, Sb, Mg or Si. Cf. C. A. 16, 1321.

Dynamite cartridge. E. A. HEDIN. U. S. 1,440,994, Jan. 2. Dynamite cartridges are enclosed in coated carbonaceous paper contg. 16-18% of a loading material such as china clay, talc, CaSO_4 or BaSO_4 which serves to avoid generation of dangerous amts. of CO from the paper when the cartridges are used.

Detonating fuses. WALTER FRIEDERICH. Can. 226,015, Nov. 14, 1922. Fuses, with a spun covering of hemp, jute, cotton, etc., which transmit detonations rapidly are made with explosives or mixts. thereof which can be readily initiated but which do not belong to the class of initial igniters. Black powder may be added to make the fuse slow burning. The covering may be waterproofed with paraffin, tar, etc.

Composition for railway signal fuses. E. C. PREN. U. S. 1,441,878, Jan. 9. A fusee which burns uniformly under all weather conditions and is capable of remaining lighted when thrown from a rapidly moving train is formed of a tough fiber tube contg. a mixt. of KNO_3 22, S 25, $\text{Sr}(\text{NO}_3)_2$ 130, rosin 4, red gum 3 and charcoal 3 parts which is not subject to spontaneous ignition.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Color matching as a factor in accurately rating the relative values of dyestuffs. H. S. BUSBY. *Am. Dyestuff Rept.* 12, 17-21 (1923).—By color matching is meant a group of methods of optical-physical measurement including colorimetry, photometry, spectroscopy, etc., which are necessary to the colorist if he is to accomplish accurate esvn. of the small differences encountered in color solns. and dyed materials, as well as the nature of these differences.

L. W. RIGGS

Sulfur dyes prepared from xylan. E. R. DARLING AND R. E. ARMSTRONG. *Am.*

Dyestuff Rept. 12, 35(1923).—Xylan or wood gum may be obtained from wood but corn cobs furnish the best raw material. Xylan is prepd. by autoclaving the coarsely ground cobs with 3% NaOH soln. under 10 lbs. pressure for 1 hr. The resulting mass is filtered and the residue given a slight wash. The liquors are united and H_2SO_4 is added until there is an excess of 2% when a ppt. forms which is filtered off and treated with hot 5% H_2SO_4 to convert it into a dark brown brittle mass; this is washed, dried and powdered. Black dye is made from xylan 200, Na_2S 825 and S 270. To this mixt. water is added to give a soln. which is slowly heated until it becomes a paste. It is then heated in an oven up to 190° and held at that temp. for 6 hrs. when the mass is dissolved in water, the dye pptd. by dil. H_2SO_4 , filtered out, washed and dried. A blue dye was made by treating the xylan with HNO_3 (50%) until the dense fumes of the N oxides ceased to be evolved and the xylan had turned yellow. The whole was then filtered, washed and at once used as in the prepn. of the black dye. L. W. RIGGS

Vat dyes of the azo series. D. N. MUKERJI. *J. Chem. Soc.* 121, 2879–82(1922).—This work was undertaken to discover a method by which insol. azo dyes could be fixed on textile fibers. $p,p'-(\text{O}_2\text{NC}_6\text{H}_4\text{NH})_2$ was absorbed by wool from dil. alk. soln. and on exposing the fibers to the air the corresponding $(\text{O}_2\text{NC}_6\text{H}_4\text{N})_2$ was regenerated within the fibers but the dyeings were not so fast to washing and alkalis as expected. Very little of the dyestuff was taken up by cotton. *p-Nitrobenzene-4-nitro- α -naphthol*, brick-red needles from $\text{PhNO}_2\text{-AcOH}$, m. 255° (decompn.). It is practically insol. in alkalis but gives a violet soln. in concd. H_2SO_4 . The *hydrazo compound* was prepd. by reduction with NH_3 and H_2S , brown amorphous mass, m. 220° . The alk. soln. is a bluish green which fades in the air. Wool dyed with this deriv. changed from violet to rose-red on exposure to the air. *p-Nitrobenzenehydrazo-o-nitrophenol*, m. 200° (decompn.), sol. in alkali with blue color; wool dyed with this compd. changed from violet to brown in the air. *4-Nitronaphthalene-4-nitro- α -naphthol*, brownish red needles, m. 240° (decompn.). This method of dyeing does not seem to be very promising as the dyeings have not the desired fastness. C. J. WEST

Application of vat colors in calico printing. F. WHITTAKER. *Am. Dyestuff Rept.* 12, 13–7(1923).—The increasing demand for fast color prints has necessitated the adoption of vat colors for goods such as shirtings, linings, dress goods, etc. These vat colors may be classified as the anthraquinonoid, indigoid and sulfurized anthracene and indophenyl series. Vat colors are applied by a reduction process, which involves the transformation of the insol. vat color into the sol. form and its absorption by the fiber in the presence of an alkali. The material is then washed whereupon the coloring matter is oxidized back into the insol. form, which is fast to light and to laundry treatment. Recipes are given for making up vat dyes with 6 different groups of colors. Hints on ageing, drying and washing off after treatment are given. L. W. RIGGS

The basic dyes in lake manufacture. HANS WAGNER. *Chem.-Zig.* 46, 801–2 (1922).—Review. Cf. C. A. 16, 3761. F. A. WERTZ

Physical chemistry of dyeing. Acid and basic dyes. T. R. BRIGGS AND A. W. BULL. *J. Phys. Chem.* 26, 845–75(1922); *Am. Dyestuff Rept.* 11, 447–50, 461–2; 12, 36–42(1923).—The chem. and phys. (adsorption) theories of dyeing are briefly stated. The object of this study was to investigate the dyeing of wool with acid and with basic dyes from the standpoint of the adsorption theory of dyeing as formulated by Pelet-Jolivet and Bancroft. The work was carried out rigidly, with control so far as possible of all the variables involved, but particularly the H-ion concn. of the dye bath. The effects of dyes on the adsorption of acids by wool and of acids on the adsorption of dyes were detd. quant. for typical acid dyes. The taking up of dyes by wool is adsorption and the amt. of dye adsorbed varies continuously with a change in the H-ion concn. of the dye bath. No evidence of chem. action between dyes and wool has been found. The

H electrode was used throughout to det. the H-ion concn. of the exhausted dye bath and in some cases also in the titration of free residual acid. The action of assistants is strictly in accord with the theory. The quant. exptl. results are assembled in 13 tables and are illustrated by 9 charts of curves.

L. W. RIGGS

Deep black and blue-black nigrosine. H. POMERANZ. *Seifenwleder-Ztg.* **49**, 722, 736(1922).—Three types of nigrosine are marketed: (1) fat-sol., a salt of fatty acids, frequently dissolved in paraffin and sold in lumps; (2) alc.-sol., a salt of HCl; (3) H₂O-sol., the Na salt of its sulfoacid (so-called "crystallized"). The first two types behave like true solns.; the 3rd is more colloidal and its soln. resembles the swelling of glue in H₂O. The chem. nature of nigrosine is not clear; it is probably a complex condensation product of aniline which on oxidation splits off N in the form of NH₃ and H as H₂O. According to the extent of condensation, which increases with increasing temp., it may show a violet, blue, green or black tint; the black is probably a mixt. of the other 3. The deep black variety is sold as "Concd.," which signifies increased covering power without actually being concd. Addition of metanil yellow to blue black nigrosine improves the color when used in shoe-cremes.

P. ESCHER

Carpet yarn dyeing. L. J. MAYOS. *Am. Dyestuff Rept.* **12**, 49-50(1923).—The varying demands of the trade are considered. The publication of the Nat. Aniline and Chem. Co. Inc. on the subject of the dyeing of carpet yarn is recommended as an aid in selecting, compounding and matching colors. Scouring should be thorough but not overdone by the use of too strong soap and soda solns. or by allowing the temp. to rise above 50°. Level shades for ground colors are an absolute necessity, and for their production, slow dyeing is essential. Oriental dyers made no effort to match shades with any degree of accuracy, the pleasing effects being produced by artistic weaving.

L. W. RIGGS

Removing vapors from dye-houses and bleacheries. J. F. SPRINGER. *Textile Colorist* **43**, 378-81, 449-51, 609-12, 691-4, 767-71(1921); **44**, 45-8, 120-4, 168-72 (1922).—A discussion of the various methods and app. used in removing vapors, etc., with illus.

CHAS. E. MULLIN

The chromates of lead in dyeing and calico printing. WM. B. NANSON. *Textile Am.* **37**, No. 6, 24-6(1922); **38**, No. 1, 22-4(1922).—A discussion of the properties of colors produced from chromates; the prepn., properties and tests of the various chromates and other chemicals used with them in dyeing; and formulas for dyeing and printing with chromates.

CHAS. E. MULLIN

Some special points in dyeing hosiery. JAMES STEELMAN. *Textile Colorist* **42**, 392-5, 468-70(1920); **43**, 249-53, 316-9, 395-6, 467-8, 546-8, 601-4, 671-3, 758-60, 827-9(1921); **44**, 29-32, 101-4, 252-4(1922).—Special details applying to hosiery dyeing are given for the application of the various dyestuffs of all classes to the different fibers and combinations of fibers.

CHAS. E. MULLIN

Continuous dyeing machines. ANON. *Textile World* **63**, 469-71, 531(1923).—Instructions are given for the continuous process of dyeing piece goods with S dyes.

CHAS. E. MULLIN

Catalysts in bleaching and dyeing. A. J. HALL. *Am. Dyestuff Rept.* **12**, 33-5 (1923).—Most metals increase the activity of bleach liquors, Cu, V and Fe being particularly active in this respect. Stains contg. metals such as Fe are tendered by bleaching on account of the catalytic action of the metal on the bleach liquor. Metals may hasten the oxidation of cellulose to oxycellulose. In aniline black dyeing, *p*-phenylenediamine or turpentine is employed as catalyst.

L. W. RIGGS

The preparation of hatters' fur. A chemical study of the carroting process. J. R. JOHNSON. *J. Ind. Hyg.* **4**, 325-34(1922).—The carroting process in the prepn. of felt for hats and work done on the substitution of a nontoxic substance for Hg are

reviewed. Using hair carotred by the $\text{Hg}(\text{NO}_3)_2\text{-HNO}_3$ method as a control an expt. carried out on a plant scale with the Stetson Co., at Philadelphia indicated that Cu and Zn with HNO_3 are the best substitutes for Mg. On a lab. scale J. tried various combinations of salts and acids. In no case was the hair carotred by these reagents of as good a quality as that treated by the Hg-HNO_3 method.

A. A. CHRISTMAN

Report of committee D-13 on textile materials. A. E. JURY, *et al.* *Proc. Am. Soc. Testing Materials* 22, 1, 497-500(1922).—Several revisions in definitions are recommended.

C. C. DAVIS

Measurement of breaking stresses, extensibilities and elasticities of single fibers of cotton, etc. T. BARRATT. *J. Textile Inst.* 13, 17-24(1922).

E. J. C.

Mercerization of single cotton hairs. R. S. WILLOWS, T. BARRATT AND F. H. PARKER. *J. Text. Inst.* 13, 229-36(1922).—Combed Egyptian sliver was boiled for 1 hr. in 2% Na_2CO_3 soln. Hairs taken from this were separately mounted in paper clips and placed in the special clips of the balance (cf. preceding abstract). A const. load of 50 mg. was imposed to keep the hair taut. As the breaking load was 6 to 7 g. the hair could be regarded as nearly free from tension. By suitable illumination a 200-fold magnified image of the hair was thrown on the screen. The hair was immersed in the test liquid at 15°, and the change of length calcd. from the change of length of the image. For all except the strongest lyes the change of length was nearly complete in 3 min. and this was taken as a standard time for all tests. Contraction begins in the NaOH soln. at 22° Tw., and is most rapid at 30 to 35° Tw. At 60° Tw. the penetration is very slow and the tech. mercerization of cloth with such a soln. would be very incomplete in the time usually allowed. On washing out of the lye, however, further action takes place; thus at 86° Tw. there was almost no action but on washing out there was a contraction of 2%. In the expts. at the end of 3 min. contact with the test lye each hair was well washed with cold water and the new length observed. Fibers have their max. length in lye of 10° Tw. Of lyes between 25 and 68° Tw. that at 40° Tw. gives the min. contraction; hence if it is required to print NaOH on a fabric so as to produce a greater affinity for dyes and but little shrinkage, 40° Tw. should be used. When solns. up to 52° Tw. are washed out of cotton hairs they extend in length. With stronger solns. there is a contraction additional to that produced by the lye. Increased tension of the hair tends to smooth out max. and min. and finally causes an extension in every soln. Decrease in temp. causes a greater contraction with lyes above 22° Tw. and the max. contraction at 0° is produced by 25° Tw. Slow washing out of concd. lyes results, as would be expected, in greater mercerization than rapid washing. Cf. following abstr.

L. W. RIGGS

Change in section of cotton hairs on mercerizing. R. S. WILLOWS AND MISS A. C. ALEXANDER. *J. Text. Inst.* 13, 237-40(1922).—The change in area of thin sections when acted on by NaOH was measured. Sections of scoured Egyptian sliver were cut by a method already described (cf. *C. A.* 15, 2728), and fixed to a glass slip by agar-agar of 14% strength, dissolved under pressure at 120°, and the mountant was dissolved off with acetone. The slip with the section was laid on the microscopic stage illuminated with a Pointolite lamp. The eye-piece of the microscope was replaced by a prism which projected the image of the section on a screen (magnification about 700 diams.). Sheets of paper of uniform wt. were weighed and pinned on the screen, the image of the section was projected thereon and the outlines of the sep. hairs were traced. This was done when the hairs were: dry, mercerized, washed out with water, dried, and finally when wet with water a 2nd time. Tests were also made by wetting with water before mercerizing. The tracings, which were recognizable at every stage, were cut out and stored loosely along with another sheet which had been previously weighed. After a day or two the cuttings and the loose sheet were weighed

From the variations in the wt. of the latter a correction could be made to all wts. on account of any changes in the humidity of the air, and thus the area of all sections detd. The increase in area on first wetting with water was 40 to 42%. In general the same set of sections gave results within 5% but results from different sections varied over 100%. The action of NaOH was more uniform. These irregularities were not expl. errors but were due to the difference in behavior of the individual hairs when acted on by the lye. Changes in sectional area when mercerized were 200% with 25° Tw. and about 270% with 45° Tw. After washing out the figures were 120 and 200%, after drying 90 and 125, and after wetting a 2nd time 160 and 125, resp. Changes in vol. after mercerizing and after washing out were parallel to changes in sectional area. The mercerized sections presented a mushroom or dumb bell appearance, apparently caused by the swelling of the cellulose in the interior and its pushing out over the cuticle, the latter not softening and swelling as rapidly as the interior cellulose. The mushroom shapes were prominent under the microscope, and this affords a simple test for the presence of tendering. In cases of tendering the cuticle is usually damaged and allows the inner portions to swell freely when NaOH is applied. The hairs are then found to swell abnormally in diam. without bulging at the ends.

L. W. RIGGS

● Bleaching cotton with hypochlorous acid. S. R. TROTMAN. *Chemistry and Industry* 42, 2-3T(1923); cf. C. A. 16, 1872.—Brown Egyptian cotton yarn was soaked 6 hrs. in 0.5% HCl at 40°, washed and boiled with 2% NaOH soln. and 0.4% sulfonated oil. The treated cotton was then bleached (1) with HClO, (2) with bleaching powder [b. p.] soln. acidified with boric acid, (3) with b. p. soln. exposed to the air, (4) with b. p. soln. acidified with HCl. The HClO was prepd. by passing Cl into water contg. chalk in suspension, the soln. being kept in contact with the chalk till used. The strengths of the solns. were adjusted to 1 g. of available Cl per l., and the same vol. of liquor was used throughout. The rate of absorption of Cl was most rapid with b. p. acidified with HCl and slowest with b. p. soln. in the air. The rates of absorption for HClO and b. p. soln. acidified with boric acid were identical. With b. p. soln. in the air the addition of CaCl₂ caused an immediate absorption of Cl, but the rate quickly fell again. The addition of HCl to HClO had a similar effect. The rate of apparent bleaching always followed in the same order as the rate of absorption of Cl. The final color was in every case estd. after washing and drying. In the case of HClO no sour was used but in the others washing was preceded by the usual acid treatment. The white product produced by HClO was in all cases better than that by Cl. With HClO neither the ash nor the tensile strength was affected. The cost of bleaching by HClO is slightly if any greater than with b. p.

L. W. RIGGS

Action of ozonized air on wool and on chlorinated wool. S. R. TROTMAN AND D. A. LANGSDALE. *Chemistry and Industry* 42, 13T(1923); cf. C. A. 16, 3211.—Samples of woollen yarns and fabrics were exposed to the action of ozonized air side by side under a bell jar with portions of the same materials previously chlorinated. Ozonized air was passed into the jar for 15 min. during 8 consecutive days. Microscopic examn. of the fibers showed that the outlines of the epithelial scales became gradually less marked and the scales disappeared exposing the cortex. Chlorinated wool or wool damaged in scouring was more quickly attacked than ordinary untreated wool. Destruction of epithelial scales to the extent of 25% was accompanied by a loss in felting power. Treatment with ozonized air caused in all cases an increase in the matter sol. in 0.1 N Na₂CO₃ soln. This action was also greater with the chlorinated or damaged fiber. After ozonizing the samples were washed with water and very dil. alkali and the sol. S was detd. There was a loss of S in every case, the loss being greater with chlorinated or badly scoured wool. Any process such as chlorination or alkali damage which renders the wool more sensitive to chem. action increases the rate at which it is attacked

by ozonized air. Wool damaged by ozone has properties similar to those of over-chlorinated wool.

L. W. RIGGS

The uses of lime in textile manufacturing. WM. B. NANSON. *Textile Am.* 38, No. 3, 11, 19-20; No. 4, 18-9, 61, 82(1922).—A discussion of the textile processes wherein lime is used.

CHAS. E. MULLIN

Lime and cotton. WM. B. NANSON. *Textile Am.* 38, No. 6, 29-30, 61, 63(1922).—An explanation of the action of lime in the kier boil based upon surface tension, emulsification and catalytic action.

CHAS. E. MULLIN

Some properties of commercial hyposulfites and sulfoxylates. C. S. HOLLANDER. *Am. Dyestuff Rept.* 12, 9-12(1923).— $\text{NaSO}_3\text{OSONa}$ is a white or grayish white granular substance which crystallizes from water in needle-shaped crystals, $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. This hydrate is not stable and, therefore, not a com. product. Its soln. rapidly oxidizes to $\text{Na}_2\text{S}_2\text{O}_8$. While the hyposulfite is neutral its oxidation product is acid and the acidity of the oxidation product accelerates the rate of decompn. by producing free hyposulfurous acid, which is far less stable than its neutral salts. While this decompn. through atm. oxidation is the most important phase, the process of autoxidation is very appreciable even in the absence of O according to the reaction $2\text{Na}_2\text{S}_2\text{O}_4 \longrightarrow \text{Na}_2\text{S}_2\text{O}_8 + \text{Na}_2\text{S}_2\text{O}_4$. The presence of acids accelerates this autoxidation and reduction, and in order to make the soln. more stable a large amt. of alkali should be added which acts as a retarder to this oxidation which always takes place to an appreciable amt. Raising the temp. promotes oxidation. $\text{Na}_2\text{S}_2\text{O}_4$ is an effective O absorber and may be used in gas analysis for the removal of O. $\text{Na}_2\text{S}_2\text{O}_4$ reacts with water and CH_2O to form sodium bisulfite, formaldehyde and sodium sulfoxylate. These products can be distinguished by the soly. of the former in alc. The latter is used in the prepn. of reducing paste for discharge printing and for stripping and to a less extent in bleaching operations.

L. W. RIGGS

Zinc oxide and lithopone as a basis for paint in bleacheries and dye houses (DR PYRSTER) 26. Coloring of paper (MANN) 23. Textile applications of corn starch and its derivatives (CATHCART) 28. Complex metal compounds of indigo blue (KUNZ) 10. Some arylazoglyoxalines (PYMAN, TIMMIS) 10. Waterproofing composition [for textile fabrics] (U. S. pat. 1,441,605) 18.

HEWITT, J. T.: **Synthetic Colouring Matters. Dyestuffs Derived from Pyridine, Quinoline, Acridine and Xanthene.** Edited by E. THORPE. London: Longmans, Green & Co. 405 pp. 14s.

Dyes. DURAND & HEGUENIN, SOC. ANON. Brit. 183,123, June 27, 1922. Addition to 166,530 (C. A. 17, 886). Instead of the dianilinomethylenedi-*o*-hydroxy-arylcarboxylic acids used therein, methylenedisalicylamide or a homolog or analog is used; nitro- and chloro-derivs. also are mentioned. Examples are given.

Intermediate products; dyes. BRITISH DYESTUFFS CORPORATION, LTD., A. G. GREEN, K. H. SAUNDERS and E. B. ADAMS. Brit. 186,878, Aug. 30, 1921. Nitroso compds. of oxyalkylated arylamines are obtained by treating the parent amines with HNO_2 and, in the case of secondary amines, treating the resulting nitrosamine with acid. By condensation with hydroxy compds. oxazines are obtained, and with amines indamines, which may be converted into azines in the usual manner. Thiosulfonic acids of oxyalkylated amines are prepd. by reducing the above nitroso compds. and treating with Na thiosulfate; they are converted into thiazines in the usual way. Examples are given. Cf. 181,750 (C. A. 16, 3762) and C. A. 16, 4355.

Condensation products (for dyes) of the anthracene series. S. STEINBUCH, F.

ACKERMANN and M. UTZINGER. U. S. 1,437,783, Dec. 5. Dyes are formed by reaction between 2- β -naphthylamino-4,6-dichloro-1,3,5-triazine, 2,4-diphenyl-6-chloro-1,3,5-triazine or other 1,3,5-triazine compds. halogenated in the nucleus and aminoanthraquinone derivs., which may be substituted in the amino group, *e. g.*, 1- or 2-aminoanthraquinone, 1-amino-4-methoxyanthraquinone, or 1,4- or 1,5-diaminoanthraquinone, 1-amino-4-chloroanthraquinone, 1-amino-4-hydroxyanthraquinone, 1-amino-2-methyl-4-toluidioanthraquinone, 1-amino-4,5,8-trihydroxyanthraquinone, 1,8-diaminoanthraquinone, 1,5-diamino-4,8-dihydroxyanthraquinone, or 1-amino-1,1-dianthrimide. Dyes of various red, yellow and brown shades are obtained.

Soluble stable vat-dye mixtures. K. THIESS and F. GLOY. U. S. 1,440,037, Dec. 26. A stable, dry and readily sol. compn. is prepd. by evap. an aq. mixt. of alkali metal salts of leuco quinone vat dyes and leuco halogen indigo, *e. g.*, a mixt. of molasses, hydrosulfite, monobromo-indigo-white, NaOH and the reduced yellow dye obtainable from quinone and *p*-chloroaniline.

Dyeing threads or filaments of cellulose acetate. L. G. RICHARDSON. U. S. 1,442,631, Jan. 16. Threads, filaments or fabrics of cellulose acetate (especially acetates lower than "triacetate") are prepd. for dyeing by subjection to a limited alk. sapon. in an aq. bath contg. NaOAc.

Dyeing cellulose acetate. E. P. SISLEY. U. S. 1,440,501, Jan. 2. Cellulose acetate articles, *e. g.*, artificial silk, are prepd. for dyeing by treatment with a dil. hot alk. soln. of Na phosphate.

Dyeing cellulose acetate. R. CLAVEL. Brit. 187,964. In the production of azo dyes on the fiber or material of cellulose acetate silk, films, etc., *sol* salts are added to the baths contg. the parent amines or the developers or to both; suitable salts are the chlorides of NH₄, Na, K, Ba, Ca, Mg, Zn, or Sn, or sulfates of Na, K, or Mg. Protective colloids, such as gelatin, boiled-off liquor, soaps, Turkey red oils, etc., may also be added when the bases or developers are used in neutral or alk. baths. *E. g.*, acetate silk is first treated in a bath contg. dianisidine hydrochloride, MgCl₂, and Na₂CO₃, then passed to a diazotizing bath, followed by a developing bath contg. α -naphthylamine hydrochloride and NaHCO₃, after which it passes to a second diazotizing bath and a second developing bath contg. α -aminonaphthol, boiled-off liquor, and MgCl₂; a black shade is obtained. Cf. 176,535 (C. A. 16, 2417).

Dyeing animal or mixed fibers. P. ONNERTZ and A. PETERS. U. S. 1,441,240, Jan. 9. In dyeing animal or mixed fibers in an acid bath with "alkali blue 4B," "zambesi black D" or similar dyes which settle out in the presence of acid, sulfite cellulose waste liquor is added to the bath to avoid or diminish settling. Na ligninsulfonate, "cell pitch" or sugars also may be used.

Apparatus for dyeing skeins. P. A. WAGNER. U. S. 1,441,898, Jan. 9. Skein carriers are mounted to travel with flexible belts.

Vat and beams for dyeing yarn. J. H. THOMPSON. U. S. 1,440,251, Dec. 26.

Autoclave. P. D. SCHENCK. U. S. 1,440,109, Dec. 26. Autoclaves adapted for use in the manuf. of dyes are formed with a lining of a Si-Fe compn. ("duriron") or similar acid-resisting material and a cast outer shell of material of greater strength and substantially the same coeff. of expansion, *e. g.*, an alloy of Cu 87 and Al 13%.

Ferrocyanides. SILVER SPRINGS BLEACHING & DYEING CO., LTD. and A. J. HALL. Brit. 188,208, Nov. 11, 1921. The waste liquor from aniline black dyeing in which ferrocyanide is used is treated with FeSO₄ so that the liquor is acid or neutral, and the pptd. blue is sepd. The ppt., which is of no value as a pigment, is dissolved by treatment with an alkali, alk. earth or NH₃, a hydroxide of Fe being also produced. To the liquor is then added an excess of an org. or inorg. acid, or first a ferrous or ferric salt and then excess of the acid, when a blue ppt. is obtained which is a good pigment.

Treating cotton bales. INTERNATIONAL COTTON PROTECTING CO. Brit. 187,394, Aug. 25, 1921. Cotton bales are proofed against fire and moisture by superficial impregnation, preferably with a soln. of boric acid contg. a small proportion of a non-coloring fixing agent such as the sulfate or other sol. salt of Zn, Sn, or Al. The boric acid may also contain a trace of H_2SO_4 . Impregnation is effected by dipping the surfaces of the bale in a shallow layer of the liquid, or in some cases by spraying.

Bleaching yarns, etc. C. BOCHTER. Brit. 187,575, May 25, 1922. Addn. to 180,325 (C. A. 16, 3403). The process described in the principal patent is modified by using in conjunction with bisulfite solns., volatile bases sol. in H_2O , such as NH_3 , $(NH_4)_2CO_3$, dimethylamine or pyridine, or salts thereof, such as NH_4HSO_3 . The volatile bases may be added to one or more of the bisulfite solns., or the linen may be impregnated with a soln. of a volatile base and then be placed in the bisulfite soln. The linen is subsequently treated with oxidizing bleaching agents such as Ca or Na hypochlorite, H_2O_2 , or alkali or alk. earth peroxide, or a per salt or mixts. thereof. The process is applicable to the bleaching of half linen.

Artificial threads, etc.; viscose. GLANZFADEN AKT.-GES. Brit. 187,942, May 20, 1922. In the manuf. of artificial threads, etc., from an unripened viscose by employing an acid coagulating bath, the CS_2 contained in the freshly pptd. acid threads is removed by treating the threads, without previous washing, with an alk. bath. The threads may be in the form of hanks or layers of yarn, the bath may be maintained at 60° , and to it may be added a small quantity of Na_2S so as simultaneously to remove the S_2 in that case, only a single washing is necessary.

Artificial silk from nitrocellulose. E. BINDSCHEDLER and J. JUER. U. S. 1,441,203, Jan. 9. Clear, unclouded products are obtained from nitrocellulose by dehydrating nitrocellulose hydrate by the action of EtOH, dissolving it (while still contg. EtOH) in dry acetone or a homolog, forming it and then drying in air contg. not more than 50% of moisture. U. S. 1,441,204 specifies extg. the acetone or homologous solvent by immersion of the formed product in C_6H_6 , dil. H_2SO_4 , concd. $CaCl_2$ soln. or other liquid which is mixable with the acetone or equiv. but which does not dissolve nitrocellulose. U. S. 1,441,205 relates to removal of the acetone by immersing the formed nitrocellulose product contg. it in a concd. soln. of $NaHSO_3$ or other compd. which will react with the acetone but not with nitrocellulose.

Mercerizing cotton yarn. A. NELSON. U. S. 1,441,740, Jan. 9. Rovings of slightly twisted cotton yarn are arranged side by side to form a chain without twisting the rovings together spirally on the axis of the chain and the chain of rovings is then subjected to mercerization under tension. Arrangement of the material in this manner serves to facilitate handling and avoid forming of knots.

Composition for rendering fabrics translucent. H. J. SUBB. U. S. 1,441,952, Jan. 9. A compn. for rendering fabrics translucent is prepd. by mixing gelatin with H_2O and adding yeast, alum and Pb acetate.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

Zinc oxide and lithopone as a basis for paint in bleacheries and dye houses. BARRINGTON DE PUYSTER. *Color Trade J.* 11, 223-4 (1922).—Tables are given showing: cc. of vehicle per g. of pigment at painting consistency, wt. of pigment required to hide, and relative hiding power of equal masses; ratio of pigment to oil, hiding power of pigment in sq. cm. per g., and hiding power of paint in sq. ft. per gallon. Zn compds. appear best as regards color retention and protection from steam and vapors.

CHAS. E. MULLIN

Manufacture of printing inks. B. G. RANSOM. *Pulp Paper Mag. Can.* **21**, 129-43 (1923).—A general discussion with special reference to the use of ink in printing, including printing requirements, intaglio, poster, book, half-tone and cover printing, process inks and news ink. C. J. WEST

Numerical tabulation and comparison of varnish tests. J. A. FINDLEY. *Proc. Am. Soc. Testing Materials* **22**, I, 479-82 (1922).—Suggestions are offered in an attempt to develop uniform varnish tests which can be interpreted accurately and will give the relative merits of varnishes for any use on a numerical basis. C. C. DAVIS

Boiled and polymerized linseed oil and other oils used in the manufacture of enamel and varnish paints. MAURICE DE KEGHEL. *Rev. prod. chim.* **25**, 613-8, 757-64, 829-38 (1922).—A description of the methods of prepn. of boiled and polymerized linseed oil, China wood oil, perilla oil, and soy-bean oil, of the properties of copal, dammar and sandarac, and of the prepn. of enamel and varnish paints, "zapon" and "cellon" varnishes, and black asphalt varnishes. A. P.-C.

Apparatus for emulsion and demulsibility tests for oils. F. WILBUR SHULENBERGER. *Paint, Oil, and Chem. Rev.* **74**, 10-11 (1922).—A brief review of the significance of the tendency of an oil to emulsify with H_2O , and of the demulsibility tests of Hershel (Bur. Standards, *Tech. Paper* No. 86), and of the U. S. Bur. Mines (*Tech. Paper* No. 298). F. A. WERTZ

The condensation products of naphthalene and formaldehyde. J. H. FRYDLENDER. *Rev. prod. chim.* **25**, 653-5 (1922).—A review of patents with a brief discussion of the merits of artificial resins and comparison of phenol and naphthalene condensation products. A. P.-C.

Amber and the dammar of living bees. MURRAY STUART. *Nature* **111**, 83-4 (1923); cf. Cockerell, *Nature* **109**, 713 (1922).—*Trigona leviceps* is the chief source of Burmese dammar. These bees build in hollows within trees, crevices among rocks etc., and line the interior surfaces of their nests with dammar. The resin is probably constructed by the bees from the oil and resin of *Dipterocarpus*. BENJAMIN HARROW

Spirits of turpentine and its substitutes. MAURICE DE KEGHEL. *Rev. prod. chim.* **26**, 1-10 (1923).—Review of the chemistry of spirits of turpentine, wood turpentine, rosin oil, sulfite turpentine, "turpentine," "terpentix," "pinex-terpentinol," white spirits, tar and gas oils, benzene, benzine, sangajol and terpine, and tetralius and dekalin, more particularly as regards their use in the manuf. of varnishes. A. P.-C.

Analytical methods in phenol-formaldehyde condensate manufacture (ORMANDY, CRAVEN) **7**. Nature of shellac (HARRIES, NAGEL) **10**.

GARDNER, H. A.: **Physical and Chemical Examination of Paints, Varnishes and Colors.** Washington, D. C.: Scientific Section, Paint Manufacturer's Assoc. of the U. S. 215 pp. \$9. Reviewed in *Ind. Eng. Chem.* **15**, 104 (1923).

KEGHEL, MAURICE DE: **Les encres, les cirages, les colles et leur préparation.** Paris: J. B. Baillière et Fils. 384 pp. 10 F. Reviewed in *Nature* **110**, 731 (1922).

TRUELOVE, RUPERT H.: **Oils, Pigments, Paints, Varnishes, etc.** London: Sir Isaac Pitman & Sons, Ltd. 2s. 6d. Reviewed in *Chem. Trade J.* **71**, 584 (1922).

Paint. P. PETERS. U. S. 1,441,168, Jan. 2. A paint adapted for use on metals to protect them from rust and for use with asbestos in insulating compus. is formed of finely ground product obtained by heating metal dross contg. Pb to near the m. p. of the latter in O or air, mixed with $CaCO_3$, SiO_2 and a binder.

Vehicle for paints. W. G. HALL. U. S. 1,439,887, Dec. 26. One cord of the wood of *Pinus palustris*, *Pinus australis* or *Pinus caribaea* is mixed with 100 lbs. of flaxseed

meal and 50 gals. of H_2O , the mixt. is subjected to distn. and light oil and residual oil obtained are mixed together to prep. a paint vehicle which forms non-blistering paints.

Chrome pigment. N. UNDERWOOD. U. S. 1,441,612, Jan. 9. $PbSO_4$ and $K_2Cr_2O_7$ are agitated in boiling H_2O together with $Mg(OH)_2$, the pigment is filtered out and the filtrate is treated with KOH to regenerate $Mg(OH)_2$ for further use.

Fireproof paint. P. OOSTERHOUSE. U. S. 1,442,089, Jan. 16. A paint adapted for use on wood or other materials is formed of calcined magnesite 4 6, powd. $MgCl_2$ 4-6, silic 8-10 parts and H_2O or other suitable vehicle.

Inks; paints. PLAUSON'S (PARENT Co.), LTD. Brit. 187,732, July 30, 1921. In making ink, water-color paints, etc., an insol. base is subjected to high-speed intensive mech. disintegration with H_2O to form a colloidal soln., to which is added a relatively small quantity of org. dye. The base used may be clay or zirconia; this, being opaque and in colloid form, absorbs the dye to form a product of high coloring power. The base is treated with H_2O in a colloid mill such as described in 155,836 and then, after settling, is again treated in the mill with a sol. org. dye in the presence of a protective colloid, e. g., gum arabic, to counteract the pptg. action of electrolytes in the H_2O , and, if copying ink is being prepd., glycol, glycerol, etc., may be added. A small quantity of disinfectant may be added to prevent decompn. of the protective colloids. After standing for a time the ink is bottled. Instead of a colorless base, colored insol. substances such as ultramarine or lakes may be used in the colloidal state with a correspondingly less amt. of dye. For India ink or water-color paints, colloids such as cherry-tree gum may be added, and colloidal clay or colloidal carbon used as the mineral base. If tannate or gallate of Fe is used as the sol. ink base, an aniline dye is added to give the desired color until the Fe salt is oxidized.

Ink. K. J. SMIDT and R. JAEGER. Brit. 187,537, Feb. 13, 1922. Printing ink is made by treating waste sulfite-cellulose lyes with HNO_3 and a catalyst, preferably metallic Cu or Zn, the product being used with coloring matters such as Prussian blue and cinnabar, or being treated with H_2SO_4 before the first reaction is completed to produce a black ink.

Ink. H. W. DOUGHTY. U. S. 1,439,695, Dec. 26. A printers' ink is formed of a resin soln. in benzyl alc. or terpineol or other volatile solvent having a b. p. of at least about 200° , together with pigments, e. g., bronze powder. U. S. 1,439,696 specifies a printers' ink contg. terpineol, ordinary rosin and bronze powder or other pigment.

Indelible ink. R. CROSS. U. S. 1,441,664, Jan. 9. An ink adapted for indelible writing is formed of H_2O , Prussian blue, oxalic acid, methylene blue and NH_4 molybdate.

Overlays for half-tone cuts. ST. PAUL JOHNS. U. S. 1,441,283, Jan. 9. An inked proof is powdered with fine emery and rosin mixt. or other powder which will intimately combine with the ink and the proof is then dipped in a soln. of Na silicate further to set the ink and powder and is then permitted to dry.

Varnishes. A. J. DISBURY. Brit. 187,847, Oct. 31, 1921. A compn. for dressing worn leather, etc., is made by combining the following mixts.: (1) gum arabic and gum copal dissolved in methylated spirit; (2) collodion dissolved in ether-acetone mixt. and methylated spirit; (3) castor and linseed oils.

Varnish. H. PLAUSON. Can. 226,633, Nov. 28, 1922. A phenol is condensed with HCHO and a vinyl compd. in the presence of a common solvent.

Dope for airplane fabrics. H. ROSS. U. S. 1,440,178, Dec. 26. Cellulose acetate together with about half its wt. of triphenyl phosphate is dissolved in solvents of different b. p., e. g., acetone, MeOAc and propylene chlorohydrin.

Artificial phenolic resins. A. HEINEMANN. U. S. 1,441,961, Jan. 9. See Brit. 184,984 (C. A. 17, 218).

27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

Two uncommon animal fats. WM. N. RAE. *Analyst* **47**, 510-11(1922).—The fat of the Ceylon bear has the following consts.: $d_{15.5}$ 0.9146, butyrefractometer at 40°, 47.2, acid no. 2.31, sapon. no. 197.0, I no. 58.7, unsapon. 0.09%. Consts. of the fatty acids are: solidifying point 37.7°, neutralization no. 207.4, I no. 55.4, butyrefractometer at 40° 35.8. The fat of cabaragoya, a large species of iguana, has the following consts.: $d_{15.5}$ 0.9142, butyrefractometer at 40°, 49.7, acid no. 2.19, sapon. no. 196.0, I no. 63.4, unsapon. 0.84%. The fatty acid consts. are: solidifying point 38.0°, neutn. no. 207.9, I no. 60.1, butyrefractometer at 40°, 40.7. E. SCHERUBEL

Catalytic hydrogenation with nickel. Factors determining catalytic activity. R. THOMAS. *J. Soc. Chem. Ind.* **42**, 21-6T(1923).—To obtain max. activity in prepg. Ni catalyst from $\text{Ni}(\text{OH})_2$ by reduction with H the temp. of reduction should be 300° in the case of an unsupported catalyst, and between 350° and 500° with Ni supported on kieselguhr. A Ni catalyst prepd. by reduction with charcoal at 600° less than $\frac{1}{4}$ as active as a catalyst reduced by H at 300°. Reduction with charcoal at 650° is complete in a short time, but the activity is less than $\frac{1}{2}$ that obtained by reduction at 600°. The activity of catalysts prepd. by elec. comminution under conditions which give the most active prepn. is not more than $\frac{1}{4}$ that of a supported catalyst prepd. by reduction in H at 350°. If currents higher than 8 amps. are used the Ni is not as finely divided and its activity falls below that given above. The activity of Ni prepd. by decompn. of $\text{Ni}(\text{CO})_4$ is little more than $\frac{1}{4}$ that of Ni on kieselguhr. Ni catalyst prepd. by replacing Ni from soln. by Al is about $\frac{1}{8}$ as active as Ni obtained by reduction with H on kieselguhr at 350°. Ni prepd. by mech. abrasion shows considerable activity at the beginning of hydrogenation and its activity depends on its large surface. Sensitiveness to temp. is one of the factors of catalytic activity; Ni reduced at 300° will absorb 4 times its vol. of H at 200° while Ni reduced at 600 to 700° has no adsorptive power for H and no catalytic activity. Neither adsorption nor intermediate compd. formation alone brings about acceleration of reaction activity but merely brings about the possibility of acceleration by bringing the reactants within the sphere of influence of the catalyst, such a sphere being a layer of mol. thickness on its surface. Negative catalysis and poisoning action are explicable on the grounds of adsorption. Ni adsorbs CO as readily as H and the film of CO adsorbed is stable owing to chem. attraction; hence 0.5% of this gas in H lowers the rate of hydrogenation to $\frac{1}{3}$ its normal value. Various considerations indicate that there is a connection between contact catalysis and the emission of electricity from the heated catalyst. Most substances which act as catalysts emit either + or - ions under temp. conditions at which they are active. Ni, under conditions employed for hardening oils, is capable of ionizing the H, for metals emit + ions at temps. as low as 190°. E. SCHERUBEL

Selective hydrogenation. T. P. HILDRITCH AND C. W. MOORE. *J. Soc. Chem. Ind.* **42**, 15-17T(1923).—Selective hydrogenation means the preferential satn. of 1 or more double bonds in compds. contg. several unsatd. centers; and this is the normal course of catalytic hydrogenation of a neutral unsatd. mixt. The following oils were hydrogenated at 180° and the values of several samples of each tabulated for m. p., I no. of oil, of the mixed acids, and of the unsatd. acids, also % of unsatd. acids and compn. of the mixed acids as % satd., % oleic, and % linoleic: Cottonseed oil with Ni and with Cu; ethyl esters of cottonseed-oil acids with Ni and with Cu; cottonseed-oil fatty acids with Ni; maize oil with Ni; soy-bean oil with Ni; linsced oil with Ni. The results show that the amt. of satd. derivs. present does not increase until the amt. of linoleic derivs. has fallen to 10% or even less of the mixt. Correspondingly the % of oleic derivs. increases at the expense of the linoleic compds. up to the same point. E. SCHERUBEL

Oils and fats from the seeds of Indian forest trees. I, II, III, IV, V. MADYAR GOPAL RAU AND J. L. SIMONSEN. *Indian Forest Rec.* 9, 95-109 (1922).—The seeds of *Chloroxylon swietenia* yield 16% of non-drying oil. The acids present as glycerides are stearic, palmitic, myristic, oleic and linolenic. Consts. of the oil were d_{40} 0.909, n_D^{20} 1.473, sapon. no. 184, I no. 84.3, R.-M. no. 0.1. The seeds of *C. wightianum* yield 34% of oil contg. 10% resin. The acids present as glycerides are stearic, palmitic, oleic and linolic. Consts. of the oil were d_{41} 0.9347, n_D^{20} 1.477, acid no. 38.3, sapon. no. 161.7, R.-M. no. 0.2, I no. 92.9, titer 20.5. The seeds of *Mimusops eelengi* yield 16% of oil contg. stearic, palmitic and oleic acids and possibly a small amt. of behenic acid. Consts. of the oil were: d_{43} 0.9113, n_D^{20} 1.4655, acid no. 2.2, sapon. no. 188.0, acetyl no. 12.0, I no. 82.2, titer 24.5°, unsapon. 1.3%. The seeds of *Shorea robusta* yield 16.4% of fat resembling Borneo tallow and contg. stearic and oleic acids. Consts. of the fat were: m. 26.5°, acid no. 14.0, sapon. no. 181, I no. 36.0, R.-M. no. 0.5, unsapon. 0.32%. *Garcinia cambogia* seeds yield 31% of fat contg. stearic and oleic acids. Consts. of the fat were: m. 29.5°, acid no. 5.0, sapon. no. 203.5, I no. 52.5, R.-M. no. 0.2, unsapon. 1.0%, titer 51.2°. H. SCHERUBEL.

The catalytic decomposition of vegetable and animal oils. A. MAILHE. *Chaleur et industrie* 3, 1144-6 (1922); *Chimie et industrie* 8, 1292 (1922).—Various oils were passed over a catalyzer (electrolytic Cu mixed with a dehydrating agent) heated to 550-650°, and yielded gases, liquid decompn. products distg. below 220°, and a residue which was subjected a 2nd time to catalysis. The liquid products of decompn. contain a small amt. of acids and a large proportion of unsatd. compds. By hydrogenation in the presence of Ni at 180°, M. obtained a colorless liquid with a gasoline odor, which was rectified. *Linseed oil* gave 2 main fractions which yielded $C_6H_5NO_2$ and $C_6H_5Me(NO_2)_2$, m. 70°, on nitration. Under the same conditions *colza oil* gave $C_6H_5(NO_2)_2$, $C_6H_5Me(NO_2)_2$, and trinitro-*m*-xylene. The decompn. products of *colza oil* consisted of methane hydrocarbons, small quantities of cyclohexane-hydrocarbons, and especially aromatic hydrocarbons. *Arachis oil* behaved in about the same manner as *colza*. *Shark oil* gave a mixt. of methane and cyclic hydrocarbons in which were identified C_6H_6 , C_7H_8 , cyclohexane, and methylcyclohexane. The gases always contain acrolein due to the decompn. of the glycerol, but consist mainly of CH_4 (38%), methane hydrocarbons (31%), and H_2 (15%). A. P.-C.

Catalytic decomposition of castor oil. A. MAILHE. *Compt. rend.* 176, 37-9 (1923).—The oil decompd. at 550° to 570° in a Cu tube contg. Al yielded H_2O , acrolein, gas and hydrocarbons. The compn. of the gas was: 18% CO_2 , 21% CO, 36% C_2H_2 , 17.3% C_2H_4 , and 7.5% CH_4 . The hydrocarbons were sepd. at 250°, and the residue passed over the catalyzer again gave light products which when neutralized with soda gave a yellow liquid with the odor of enanthone. The exptl. results show that the decompn. of castor oil is different from that of other vegetable oils in that epanthylid aldehyde is formed; the hydrocarbons formed below 600° belong to the methane series and those formed above 600° belong to the aromatic series, such as benzene, toluene, and *m*-xylene; since the decompn. is effected with pieces of Al in a Cu tube there is no free C formed; ethylenic acids are formed. H. SCHERUBEL.

Evolution and future of the Tunisian oil industry. GEORGES RAY. *Chimie et industrie* 8, 1318-31 (1922).—A description is given of the methods used for the production of olive oil (native and European processes). A. P.-C.

The coconut-oil industry of Marseilles. HENRI BLIN. *Mat. grasses* 15, 6334-7 (1923).—Description of the process used at Marseilles for the extrn. and refining of coconut oil. A. P.-C.

Wax coating the stems of the Australian cane grass, *Glyceria ramigera*. F. v. M. H. G. SMITH. *J. Soc. Chem. Ind.* 41, 372T (1922).—This wax resembles carnauba

wax. It m. 82° , acid no. 54.2. It is insol. in H_2O , slightly sol. in alc. benzene, acetone and $CHCl_3$ in the cold, but dissolves in all of them when boiled. The part insol. in cold ether is also insol. in boiling ether. The ether-sol. portion had d_{18} 0.975 and the insol. portion d_{18} 0.9819. The sapon. no. of the ether-insol. wax was 89.4 and of the esters 35.1.

F. SCHRRUBEL

Soap manufacture and the Calcutta Soap Works, Ltd. A. N. PALIT. *J. Indian Ind. Labour* 2, 489-95(1922).—Brief outline of the development of the Indian soap industry, with a description of the plant mentioned.

A. PAPINEAU-COUTURE

White soda soft soaps. I. P. Seifensieder-Ztg. 49, 623-4(1922).—Five formulas are given for prepg. soft soaps, made from NaOH or mixts. of NaOH and KOH and filled with water glass and soda ash, to take the place of the more expensive pure KOH soaps.

P. ESCHER

Significance of the oxidized fatty acids. JOS. GROSSER. *Seifensieder-Ztg.* 49, 635-7(1922).—Oxidized fatty acids usually enter the lye in the soap kettle, especially when it contains an excess of alkali, as much as 0.94% having been formed. They are insol. in petroleum ether (hydroxy acids are sol.) but a portion may become sol. in the presence of a concd. soln. of fatty acids from fish oils; they may be re-pptd. from such a soln. by diln. with more petroleum ether. They are the carriers of the dark coloring matter of oils. The value of "degras" oils, used in tanning, depends upon their content of oxidized acids, which aid emulsification in H_2O . In the distn. of fatty acids the oxidized acids remain largely behind in the tar, only a portion distg. over and causing subsequent darkening. Oxidized acids, hydroxy acids and rosin acids are similar in the soly. of their alkali salts in H_2O and of the free acids in alc.

P. ESCHER

Preparation of active Ni catalysts (BROCHET) 2. Viscosity of soap solutions (CLARK) 2. Dehydrating oil in storage tanks (U. S. pat. 1,440,352) 22.

HOLDE, D.: Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes. 2nd Ed. revised. Edited by E. Mueller. New York: John Wiley & Sons. 572 pp. \$6. Reviewed in *Proc. Am. Soc. Civil Eng.* 48, 732(1922).

Viscous oily compositions. PLAUSON'S (PARENT Co.) LTD. Brit. 186,950, April 13, 1921. Wax or crude bitumen, such as ozocerite, beeswax, montan wax, carnauba wax, or Japan wax, is treated with an aldehyde, such as $HCHO$ or furfural, in presence of an alkali, with or without addn. of a ketone, such as acetone or methyl ethyl ketone, or a dihydric or trihydric alc., such as glycol or glycerol. The product, after removal of the alkali by washing, may be added to mineral, tar, animal or vegetable oil, yielding viscous or paste-like products which may be used as lubricants or cosmetics, or emulsified with H_2O forming *salves* or *leather-dressing compns.* It may be mixed with 20-30% of paraffin wax, ceresin, ozocerite, etc. without affecting its properties. Instead of aldehydes, their polymerization products or substances, such as hexamethylenetetramine, capable of liberating aldehyde may be used.

Refining fatty acids. J. W. BODMAN. U. S. 1,439,685, Dec. 26. Dark-colored fatty acids, e. g., refinery foots for soap making, are subjected to evapn. and the vapors are commingled with superheated steam. This mixt., flowing at high speed, is subjected to centrifugal action (induced by whirling) at a temp. above the distn. point of the fatty acids and is thus freed from particles of pitch or other impurities. After this treatment, light colored fatty acids are liquefied in a condenser and recovered.

Extracting fats, etc.; distilling fatty acids, etc. S. ZIPSER. Brit. 186,040, July 27, 1922. In the extn. of fats, etc., by volatile solvents, air is excluded and the varying pressure due to the movement of fluids in the plant is corrected by the flow of H_2O in

or out of a tank connected to the separator of the condensed steam and solvent. H_2O may also be run from the tank to reduce the pressure throughout the plant, and any gas, such as air admitted during charging of the extractors, contg. vapors not liquefied by the condenser, is returned to a freshly charged and preferably evacuated extractor for absorption of the vapors by the charge. A suitable app. is specified.

Rotary horizontal tank adapted for rendering fats with steam. W. LISTER. U. S. 1,432,028, Oct. 17.

Treating cottonseed. M. O. PARTINGTON. Brit. 186,943, Nov. 30, 1921. The fiber adhering to cottonseed is removed by treating the seed first in a beater, then in a rotary cleaning app. and then passing it from end to end through a bath of H_2SO_4 or HCl or caustic alkali and finally cleaning and drying. A suitable construction is specified.

Soaps. P. KREBITZ. Brit. 186,960, June 3, 1921. The lime sludge obtained by the action of soda on a lime soap is treated to remove residual soap by adding soaps of palm-kernel oil, coconut oil, or resin. The sludge is then lixiviated with H_2O or weak salt soln. and the lime carbonate filtered from the soapy soln. Palm-kernel oil soap or coconut oil soap is added in such quantities so as to amount to not less than 25% of the total soap in the sludge after the addn., and resin soap to a corresponding min. amt. of 20%. If the residual soap is wholly or mainly palm-kernel oil soap or coconut oil soap, this addn. is unnecessary.

Soap pastes. M. T. KHORASSANY. Brit. 187,660, June 22, 1921. A fat stock, e. g., a mixt. of equal parts of coconut or palm oil and pressed tallow, is saponified with a considerable excess of soda lye, amounting preferably to 1-2 parts by wt. of $NaOH$ to 1 part of fat. From $1/3$ to $1/4$ of the excess $NaOH$ may be replaced by its equiv. of Na_2CO_3 . Preferred quantities for 1 kg. of fat are $NaOH$ 0.750, Na_2CO_3 0.265, and H_2O 8-10 kg. The saponified mixt. is concd. with const. stirring until a granular, plastic product is obtained. When required for use this product is mixed with 10 times its wt. of boiling H_2O forming a soln., which solidifies to a paste upon cooling.

Cleaning compositions. F. HULL and L. STEER. Brit. 187,526, Jan. 5, 1922. A saponaceous cleansing compn. is made by heating together about 1 cwt. yellow soap chips, 7 lb. pearlash, 7 lb. washing-soda, $1 1/2$ pts. liquid NH_3 , $1 1/2$ pts. turpentine, 1 qt. paraffin oil, with or without a perfume such as oil of almonds.

Detergent. A. J. LEONARD. U. S. 1,441,100, Jan. 2. A mixt. adapted for washing fabrics or the hands is formed of soap, H_2O , gasoline, alc., paraffin, K_2CO_3 , sugar, camphor, H_3BO_3 and oil of mirbane.

28—SUGAR, STARCH AND GUMS

F. W. ZERRAN

Report on meeting of the Society of Technical Advisers of the Java sugar industry, April, 1922. Meeting of Chemical Section. *Arch. Suikerind.* 30, Part 3, 121-57 (1922).

—This is a round-table discussion, not suitable for abstracting, on juice clarification, sirup and molasses sulfitation, Bach process, massecuites and molasses, exhaustibility of molasses, quality of Java sugar, utilization of molasses, factory control, and sampling of sugars at the ports. **Meeting of Engineering Section.** *Ibid* 159-76 (1922).—A similar report concerning the following topics: Boilers, fuel economy. **Meeting of Agricultural Section.** *Ibid* 177-219.—The subjects of chem. interest were fertilizers and diseases. **Joint final meeting.** *Ibid* 219-25 (1922).—The topic dealt with was the training of sugar-plantation employees.

F. W. ZERRAN

The sugar industry in China. ANON. *J. Assoc. Chin. & Am. Eng.* 3, 35-7 (1922).

WM. H. ADOLPH

Phosphoric acid in cane juices. H. WALKER. *Ind. Eng. Chem.* 15, 164-5; Louisi-

ana Planter 70, 127-8(1923).—Soil analysis is known not to give reliable indications about fertilizer requirements, and plant analyses have their limitations owing to the difficulty of correct sampling. But cane-juice samples truly representative of entire fields can be obtained from the crusher or first mill in the factory. P_2O_5 detns. were made by titration with $UO_2(AcO)_2$, the results of duplicates checking within 2 mg. P_2O_5 per 100 cc. juice. The P_2O_5 generally decreased with an increase of elevation of the field. Fields which yield juices with 20 mg. P_2O_5 or more per 100 cc. are probably not in need of P fertilization. With less than 20 mg. field expts. are indicated, and with less than 10 mg. the application of P fertilizer is advisable. F. W. ZERBAN

A report on the results of experiments in sugar-cane cultivation in St. Croix during the seven-year period from 1915 to 1922. EDUARD GEDDE. *Louisiana Planter* 69, 427-9, 447-9, 467-8(1922). C. H. CHRISTMAN

The histological characters of the root of the sugar beet from the point of view of selections. H. PLAHN. *Louisiana Planter* 70, 12(1923).—Selection of beet roots based upon the polarization and weight of the root furnish insufficient data. To obtain good root development in order to increase the wt. of the residue for stock feed the ratio of water to dry matter is important. By this ratio the compactness of the root can be obtained and should be less than 1:2.75. C. H. CHRISTMAN

The problem of milling low-purity cane. C. G. LEONIS. *Sugar* 24, 651-3(1922).—Poor cane with its low-purity juice often is handled at a loss. A minimum basis should be established for juice, such as 15° Brix and 70 purity. For this standard 14.35 tons of cane yield 1 ton of sugar. A plan is presented for calcg. the proceeds obtained in mills of 150-600 tons capacity and showing how much cane must be worked for a given return. C. H. CHRISTMAN

Modern views on juice clarification. H. C. PRINSEN-GEERLIGS. *Arch. Suikerind.* 30, 877-88(1922).—An address, calling attention to the colloid-chem. aspects of juice purification, with special reference to adsorption, ultrafiltration, and flocculation of the colloids. F. W. ZERBAN

Sulfured juice. E. HADDON. *Rev. agr. Maurice* 1, 248(1922).—The usual practice of considering the d. of the dil. juice to be equal to that of the sulfured juice is erroneous. The d. must be corrected by adding to the wt. of the juice that of the SO_2 added and that of the condensation water, and then dividing by the total vol. F. W. ZERBAN

Carbonatation. L. FAUQUE. *Rev. agr. Maurice* 1, 182-4(1922).—Historical. F. W. ZERBAN

Entrainment during concentration. E. HADDON. *Rev. agr. Maurice* 1, 247(1922).—With barometric condensers, and with the *vacua* used at present the Hodek catch-all (*C. A.* 14, 858) is not efficient enough. Following a suggestion by Helmer (*C. A.* 14, 3332) a cone of wire netting was placed in the top of the effect, and later a double cone. The sugar loss was thus cut down to traces. SO_2 , H_2SO_4 and Fe were also found in the condensate, and the glucose ratio in it was higher than in the sirup. F. W. ZERBAN

The application of the process of de Haan in the cane-sugar and in the beet-sugar industries. H. A. C. VAN DER JAGT. *Chem. Weekblad* 20, 9-15(1923).—In the beet-sugar industry the raw juice is treated with an excess of CaO; in the cane-sugar industry an excess of CaO must be avoided, according to de Haan, as this would cause a decomposing of the glucose. The purification of the juice is not due to a chem. action of the CaO, but merely to a physical action of the $CaCO_3$ ppt., formed in the juice, which adsorbs the impurities. The best results are obtained by low concns. of CO_2 . J. describes expts. with *beet sugar juice* (on a small scale) which prove that in this case also the method of de Haan can be applied. Also, in this case, an intense action of high concns. of CaO can have unfavorable results; furthermore the formation of foam

is entirely prevented because of the low alkalinity. By working with thick lime milk, some factories of cane-sugar in Java had difficulty from decompn. of the glucose; in such a case the lime milk should be dild. with dil. juice. Na_2SO_3 also causes a decompn. of glucose (similarly to dil. NaOH), although Na_2SO_3 does not produce a brown color of the glucose soln.

R. BEUTNER

Manufacture of white plantation sugar with Darco. G. AVOT. *Louisiana Planter* 70, 71-2(1923).—Liquor at 28-30° Bé. from the effects comprises 45% of the sirup used for a No. 1 strike. The balance is a sirup of 99 purity made by washing and melting second sugars. After washing this second sugar in centrifugals to 99 purity it is melted and mixed with 1/2% each of Darco and Filter Cel, boiled 5 min. and filter-pressed. The cake obtained is washed and sent to the lining station where it serves to aid defecation. A second strike is made from the No. 1. molasses and sirup from the effects and the sugar obtained is washed and melted for a No. 1 strike. The No. 2 molasses is boiled to a third strike which is worked back to a prime sugar. The washings and run off are boiled back with the second strike. A second method is more expensive. Darco is added to mill juice at the rate of 3 lb. per ton of cane. After 15 min. lime is added to 0.8 cc. acidity together with 3 lb. Filter Cel. Clarification and evapn. follow. Better yields similar to the above method are obtained. C. H. CHRISTMAN

The determination of traces of invert sugar in sucrose. I. M. KOLTHOFF. *Arch. Suikerind.* 30, 867-70(1922).—Krais's method (*C. A.* 15, 2013) is accurate only to 0.005%. The colorimetric method of Sumner (*C. A.* 15, 2647) is simpler and more certain, and can be applied to sucrose as follows: warm 2 g. dinitrosalicylic acid and 6 g. crystd. Na_2CO_3 with 70 cc. of water until soln. is complete, cool, dil. to 100 cc., and filter if necessary. Dissolve 2 g. of the sugar to be analyzed with 10 cc. warm water in a wide test tube, shaking constantly. Place for 2-3 min. in a water bath kept at 70°. Add exactly 1 cc. of the above reagent, mix, and then add 2 cc. 4*N* NaOH . Mix again and place for exactly 8 min. in the water bath at 70°. Cool, wash into a colorimeter cylinder, and compare with standards contg. known quantities of invert sugar. Also run a blank with 10 cc. of water, and apply the correction. If the invert sugar in a sample exceeds 0.015%, less sugar must be used in the test, and new standards made. All color detns. must be made as soon as possible. The amts. of reagents given and the sequence in which they are added, must be strictly adhered to.

F. W. ZERBAN

Unreckoned sugar analysis losses. C. G. LEONIS. *Sugar* 25, 6-7, 71-3(1923).—Errors in optical values introduce unaccounted losses in beet-sugar houses. Other losses arise from partial or complete destruction of the sugar by heat, entrainment and errors in direct sugar analyses. The formation of high polarizing dextrans in acid and neutral solns. introduces an error preventing a balance of sucrose entering and leaving the process. Decompn. of sucrose at higher temps. occurs in solns. approximating neutrality, the more rapidly in dil. than in concd. solns. Improper purification or over 3% raffinose in sugar favors caramel formation. Entrainment losses are greatest in the last body and vacuum pan, but may be prevented. A method of analyzing condenser water for sugar and calcg. entrainment is given in detail. C. H. CHRISTMAN

The deterioration of sugar in ware house. E. HADDON. *Rev. agr. Maurice* 1, 249(1922).—Sugar deteriorates appreciably only in humid, not in dry air, as moisture is necessary for the development of microorganisms. Sugar will take up the more moisture the smaller the crystals, on account of larger surface exposed. A high content of reducing sugars also makes the sugar more hygroscopic, and for this reason badly purged sugars full of molasses absorb moisture readily. It is advisable to pack sugar in containers made of such materials as will insulate the sugar from the humidity of the atm.

F. W. ZERBAN

Protective inoculation of raw sugar. W. L. OWEN. *Sugar* 25, 65-8(1923).—Enormous losses in raw sugar during storage are caused by molds, principally *Aspergillus repens*. The factor of safety $W/(100-S) = 0.33$ (cf. following abstr.) has been used to anticipate and avoid deterioration. Torulae are always present with molds but have not shown activity in the causing of losses. Torulae fermentation is confined to the invert sugar and selectively attacks levulose. Sugars inoculated with torulae alone showed no decrease in sucrose though the factor of safety showed that favorable conditions existed. A very small amt. of torulae exerts a distinct protective action. Inoculation of sirup of 70° Brix with mold and torulae showed much loss due to mold alone but very little loss when torulae were also present. This action of torulae in preventing mold action is ascribed to the development of CO_2 .
C. H. CHRISTMAN

A study of the factors affecting the moisture absorption of raw and refined cane sugars. W. L. OWEN. *Louisiana Planter* 70, 88-90, 107-8(1922).—The equation $W/(100-S) = 0.33$ is used to det. the keeping qualities of cane sugar, where W = moisture and S = % sucrose. Various factors affect the moisture-absorbing power of a sugar. Exptl. data indicate that moisture absorption is inversely proportional to the size of the crystal. The expts. were carried out at 30° and 100% humidity, 30° and over 10° Brix H_2SO_4 and 30° and 35° Brix H_2SO_4 . Moisture absorption is over 50% less at the lower temp. Comparison of standard granulated and plantation granulated gave greater absorption by the plantation granulated during the first 24 hours but less over a period of 96 hours. Further examination indicated that the rate of absorption as well as the final moisture content was dependent upon the initial content. Gums from Cuban molasses were pptd. with alc. and dild. to a definite vol. Solution of gums equiv. to 0.2 and 0.4% were added to sugar and dried thoroughly. These absorbed moisture using standard granulated as a check and the additional increase was 5% for 0.2% gum and 22% for 0.4% gums. Both CaO and sol. sugar ash increase the rate of absorption. The presence of reducing sugars materially increased the rate of absorption.
C. H. CHRISTMAN

The discovery and production of arabinose. T. S. HARDING. *Sugar* 24, 656-7(1922).—A detailed bibliography is given. Boiling beet pulp 1.5 hrs. with 1% H_2SO_4 is sufficient to hydrolyze the arabinose. The acid is neutralized with Ba(OH)_2 to neutrality to litmus. After standing overnight the clear liquid is decanted and the residue filtered. Basic lead acetate may be used to advantage. After deleading and concg. to 250 cc., 500 cc. alc. is added. Crystn. proceeds best from glacial acetic acid and alc. contg. 1% HNO_3 . A yield of 4-5% of the beet pulp used is obtained.
C. H. CHRISTMAN

A new method for the manufacture of baryta for treating molasses. CAMILLE DEGUIDE AND PAUL BAUD. *Compt. rend.* 174, 1177-9(1922); cf. *C. A.* 16, 3408.—About 15% of the amt. of sucrose obtained from beets is retained by the molasses. Several attempts to recover the sucrose have been discarded owing to the expensive-ness of Ba(OH)_2 . The calcining of BaCO_3 presents serious difficulties. The authors noted that tribarium silicate could be easily made by fusing SiO_2 and BaCO_3 in the mol. ratio of 1:3; and that the fused product $\text{SiO}_2 \cdot 3\text{BaO}$ liberated over 90% of $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$, depending upon the fineness of the materials and the temp. of fusion. Expts. showed the greatest yields of Ba(OH)_2 when the materials were ground to 200 mesh and fused at 1300°. The Ba saccharate is easily decompd. by CO_2 . The process represents a complete cycle, the BaCO_3 produced from the carbonation vats and the $\text{SiO}_2 \cdot \text{BaO}$ from the mixers being used over again, to produce the tri-barium silicate. Expts. on fusing 6000 kg. BaCO_3 and 600 kg. SiO_2 showed a recovery of from 70-80% Ba(OH)_2 with hot water. The filter-press liquors from the Ba saccharate contain N 1% and K_2O 6%.
ACHILLE R. ALBOUZE

Baled bagasse as fuel for locomotives. G. J. SCHORR. *Arch. Suikerind.* **30**, 858-85(1922).—Bagasse pressed into bales about 35 by 45 by 60 cm. in size can be used without trouble in firing plantation locomotives, without any change in furnace design and without appreciable loss in power developed. F. W. ZERBAN

Gas coke for sugar factories. HENRY DECLUY. *Bull. assoc. chim. suc. dist.* **39**, 501-517(1922).—Gas coke can be used as well as metallurgical coke in lime-kilns for beet-sugar manuf. The objections to gas coke, i. e., its lack of strength, its S and its ash, are groundless. Instructions for the control of lime kilns are given. (1) If there is very little CO in the exit gases with excess of O₂ and the appearance of the fire normal, there is entrance of air between the pump and the fire; or, if the fire is red, the CO₂ pump is running too fast. If possible, increase the number of charges. (2) If the CO₂ content of the gas varies, with the fire changing from dark to light between charges, the charges are too heavy and the intervals between them are too long. (3) If the gas is poor in CO₂ without excess of O₂ or CO and the fire is normal, with limestone correctly crushed, there is an excess of coke in the charge; if the lime is not crushed enough, there will be unburned pieces. (4) If there is an excess of CO without excess of O₂ and the fire is dark and the limestone properly crushed, then the pump is going too slowly or the charges are too heavy or the lime may be crumbling and the circulation stopped. Lower the upper level of the charge. If the appearance of the fire is normal, then the dissociation zone is too high because the coke is not crushed enough. (5) If there is an excess of O₂ and of CO and the fire is dark, there is a back-flow of air or the charges are too large; if the fire is normal then the coke is not broken enough. A table shows the CO₂ content of gas for a given quality of coke and limestone. W. L. McCABE

The manufacture of sodium cyanide from distillery and sugar-house residues. DEJUSSEU. *Industrie chimique* **9**, 530-3(1922).—A fairly detailed description of the Reichardt and Bueh process (D.R.P. 86,913, 87,725, 113,530, 181,508; Eng. pat. 7171 (1895); Fr. pat. 246,282, 296,793, 367,502; U. S. pat. 607,801, 720,402). A. P.-C.

Purification of sugar-factory wastes. E. ROLANTS. *Sugar* **25**, 59-61(1923).—A résumé of the previous work on the biol. purification of wastes is given. The use of bacterial beds is advocated as the most efficient method of removing sugar and nitrogenous matter from such wastes. C. H. CHRISTMAN

Plastometer tests on alkaline thin-boiling corn starches. C. E. G. PORST AND M. MOSKOWITZ. *Ind. Eng. Chem.* **15**, 166-70(1923); cf. *C. A.* **14**, 657.—Further tests were made with 7 thin-boiling starches of varying fluidity, treated with different amts. of NaOH so as to change the H-ion concn. The results are given in tables and curves. For the curves complete logarithmic equations have been calcd. The best temp. to which to heat the paste is 95°. On the addition of NaOH the pastes from thin-boiling starches first become firmer until the paste shows a p_H of 6.2-6.3, and the starch of 7.4. With increasing alk. the paste becomes weaker and smoother, and translucent. In tests with thick-boiling starches it was noted that there is no definite relationship between paste characteristics on the one hand and sol. and N content on the other, except for one and the same sample of starch. Thick-boiling starches are the better the lower their mobility. F. W. ZERBAN

Textile applications of corn starch and its derivatives. W. R. CATHCART. *Am. Dyestuff Rept.* **12**, 21-8(1923).—The processes of making corn starch, modified starches, corn sirup, corn sugar, thin and thick boiling starches such as are used in textile work are described. L. W. ROGGS

Use of molasses as fertilizer (FAUQUE)(DE SORNAY) 15. Nitrification of filter-press cake in acid red clay soils (RAMIREZ) 15.

WALLIS-TAYLER, A. J.: **Sugar Machinery.** Revised and enlarged. New York:

Book Department of *Sugar*, 153 Waverly Place. 392 pp. \$4.00 postage and duty paid. Reviewed in *Sugar* 25, 41(1923).

The regeneration of powdered, decolorizing vegetable charcoal. NAAMLOOZE VENNOOTSCHAP, ALGEMEENE NORIT MAATSCHAPPIJ. Holl. 6,919, Feb. 14, 1922. Spent charcoal used in sugar manuf. is suspended in a dil. mineral acid, kept at the b. p. and stirred till all acid-sol. impurities are dissolved. It is then sepd. and washed free from acid.

29—LEATHER AND GLUE

ALLEN ROGERS

The swelling of hide powder. III. E. C. PORTER. *J. Soc. Leather Trades' Chem.* 6, 417-25(1922); cf. *C. A.* 16, 1883.—The addn. of NaCl to solns. of acid and alkali increases the hydrolysis of hide powder more than could be accounted for by change of pH . This is attributed to activation of the H and OH ions. By a modified Sørensen titration it was found that continued hydrolysis of the collagen, after it had once passed into soln., was very slight. F. L. SEYMOUR-JONES

Chrome leather analysis sub-committee. D. WOODROFFE. *J. Soc. Leather Trades' Chem.* 6, 426-7(1922); cf. *C. A.* 16, 3229.—Samples of box calf were analyzed. Agreement between analysts was bad. The basicity of the Cr salt on the fibers of 13 samples of box and willow calf leather was detd. The basicity figures varied from 18 to 70.8%, the majority lying between 40 and 55. F. L. SEYMOUR-JONES

Committee on limeyard control. VI. The estimation of alkaline sulfides by standard zinc sulfate solution. W. R. ATKIN. *J. Soc. Leather Trades' Chem.* 6, 427-37(1922); cf. *C. A.* 16, 3230.—Distn. methods, whereby H_2S is absorbed in a suitable reagent, fail with arsenic limes, in that the Ca thioarsenite decomposes on boiling yielding H_2S and Ca oxythioarsenite, results being too high. The HCHO method (*C. A.* 16, 3230) fails with used lime liquors contg. NH_3 and protein degradation products. Running the sulfide soln. into a dil. acid I soln. fails in that Na_2S and its solns. on exposure to air lose H_2S and form $Na_2S_2O_3$. Titration with standard $ZnSO_4$ has aroused much controversy. NH_3 and NH_4Cl are added to the reacting medium to ensure the formation of a complex $Zn(NH_3)_x$ ion, so that the soly. product of $Zn(OH)_2$ is not, and that of ZnS is, exceeded. Reasoning from these considerations, a new method is devised and shown to be exptly. accurate for all cases liable to occur in practice. A stock soln. is made 0.5*N* in NH_3 and contg. 12.5 g. NH_4Cl per l. To 25 cc. of the sulfide soln. or lime liquor is added 25 cc. of this stock soln., and the mixt. is titrated with 0.05 *M* $ZnSO_4$, with Pb acetate paper as external indicator. In the calcn. of results, 1 cc. 0.05 *M* $ZnSO_4$ = 0.0039 g. Na_2S . F. L. SEYMOUR-JONES

The determination of soluble tannins by subsidence. F. C. THOMPSON. *J. Soc. Leather Trades' Chem.* 6, 438-42(1922).—In filtering tannin solns. to optical clarity for the detn. of total solubles, while sorption of sol. matter by filter papers and candles can be obviated by first satg. these with the liquor, the question of "optically clear" is one of personal judgment liable to introduce large errors between different analysts. Filtration may merge into ultra-filtration and expts. have shown that quebracho, mangrove, and gallotannin solns. can be detannized by the use of suitable membranes. To eliminate these errors it is proposed to allow the insolubles to settle out. A cylinder of 5 cm. diam. is filled to a height of 20 cm. with tan liquor and allowed to stand 2 hrs. A 50-cc. pipet is inserted with its tip exactly 5 cm. from the surface of the liquor and this is drawn off for analysis as usual. Results are generally slightly higher in total solns. than with the filtration method, the difference amounting to 12% with natural que-

brácho and 15% with hemlock bark ext. It is assumed that the settling out of the insol. particles is unaffected by the Brownian movement. **Note on the influence of the Brownian movement on the motion of a particle under gravity.** S. BRODETSKY. *Ibid* 6, 442(1922).—It is shown by mathematical analysis that the above assumption is justified.

F. L. SEYMOUR-JONES
The acidity of synthetic tans. S. KOHN, J. BREEDIS and E. CREDE. *J. Am. Leather Chem. Assoc.* 18, 21-4(1923).—An approximation of the amt. of free H_2SO_4 in a sample of syntan can be obtained as follows: The sample is appropriately dild. and an aliquot titrated against standard NaOH, with methyl orange. A second aliquot is treated with 2% gelatin soln. until no further ppt. forms and filtered, the filtrate being titrated for acidity as in the original sample. The value of the ratio of the second to the first titration indicates whether the amt. of free H_2SO_4 is large or small. But H_2SO_4 is neither the sole nor the most harmful ingredient found in some syntans; the quality of leather produced depends largely upon the nature of the sulfonic acids.

J. A. WILSON
"Purity" of tanning materials. R. O. PHILLIPS. *J. Am. Leather Chem. Assoc.* 18, 2-4(1923).—An appeal to substitute "tannin dry basis," or similar expression, for the much abused term "purity."

J. A. WILSON
The tanning extract industry of the U. S. A. LEOPOLD POLLAK. *Gerber* 1922, 75-7, 83-4, 93-4, 101-4, 128-30, 136-9; *J. Am. Leather Chem. Assoc.* 18, 12-21, 61-92 (1923).—A review of papers by American writers, largely statistical and non-chemical, dealing with sources of vegetable tanning materials and the manuf. of exts. therefrom.

J. A. WILSON
Chemical analysis of Chinese gall nut. Y. K. WANG. *Science (China)* 7, 597-601(1922).—Analyzes 17.57% moisture and 51.01% sol. tannis.

WM. H. ADOLPH
The practical color measurement of vegetable tan liquors. R. O. PHILLIPS and L. R. BROWN. *J. Am. Leather Chem. Assoc.* 18, 24-8(1923).—Measurements with the Lovibond tintometer show that a filtered tan liquor darkens in color more rapidly than one contg. insol. matter. Measurements must be made as soon as possible after dissolving the ext. in water and at definite p_H value. It is suggested that a pressed block of standard hide powder might be tanned and the color imparted to it be taken as the color value of the tan liquor used. With a set of standards, the color values could be expressed numerically.

J. A. WILSON
The gold number of commercial gelatins. F. A. BILLOTT and S. E. SHEPPARD. *J. Ind. Eng. Chem.* 13, 699-700(1921).—An attempt at the classification of gelatins by their gold nos. Zsigmondy's method (cf. *Ann.* 301, 29(1898)) for the prepn. of deep red, homogeneous Au hydrosols was modified to make this prepn. easier and more reliable. Hard, medium and soft gelatins by various methods of manuf. differed little in their protective action, and no classification could be made bearing any simple relation to useful properties. The Au no. decreased with the concn. and increased with the age of the gelatin soln. The Au no. was a function of the degree of subdivision of the gelatin. The proportion of large to small particles depended upon the equil. temp., a predominance of large particles occurring at lower temps.

C. C. DAVIS

The manifold nature of the proteins (BLACKADDER) 11A. Chinese tannin. Tannin of native oak (FREUDENBERG, *et al.*) 10. Waterproofing composition (for leather) (U. S. pat. 1,441,605) 18.

LORENZ, J. R.: **Nature and Control of Tannery Processes.** Mass., U. S. A.: Shoe and Leather Reporter. 52 pp. \$2.00. Reviewed in *J. Soc. Leather Trades' Chem.* 6, 444(1922).

Tanning. H. MORIN. Brit. 187,239, Oct. 14, 1922. Hides and skins are tanned with the double halides of Sn and another metal, preferably the double chlorides of Sn and a metal of the alkali or alk. earth group, or with a mixt. capable of producing them. The hides are immersed in a mixt. of SnCl_2 and NaCl or, if desired, the Sn halide is used first and subsequently the hides are treated with a halogen salt of another metal capable of forming a double halide. To facilitate the removal of acid after tanning, the Sn salt may be partially neutralized by a base before the double salt is prepd. After treatment, the hides are drained and then agitated in aerated H_2O until insol. basic salts are produced.

Tanning material from cellulose waste sulfite liquor. A. RÖMER. U. S. 1,441,243, Jan. 9. Waste sulfite liquor is treated with CaCO_3 or $\text{Ca}(\text{OH})_2$ to ppt. SO_3 as CaSO_3 and after removal of the ppt. the remaining liquor is treated with Na_2CO_3 to convert the sulfolignic acids from their Ca compds. into the corresponding Na compds., which are later partially decomposed by the action of HCl (in half the amt. required theoretically) to obtain free sulfolignic acids available for use in tanning.

Coated fabric for shoe vamps or gloves. E. WEINHEIM. U. S. 1,441,318, Jan. 9. A textile fabric which is stretchable in one direction but not in the direction at right angles is filled with a "leatherizing" dope and is afterward given a coating which also will permit some stretching of the finished material.

